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November 1975

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November 1975

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Proceedings of a Conference on Emerging Environmental Problems

Acid Precipitation

Sponsored by
New York State Department of Environmental Conservation
United States Environmental Protection Agency, Region II
Water Resources and Marine Sciences Center, Cornell University
Center for Environmental Quality Management, Cornell University

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PROCEEDINGS OF A CONFERENCE ON EMERGING
ENVIRONMENTAL PROBLEMS:

ACID PRECIPITATION

May 19-20, 1975
The Institute on Man and Science
Rensselaerville, New York

Published by the
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Gerald M. Hansler, P.E.
Regional Administrator

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CONFERENCE OBJECTIVES

Because of the potential long-term ecological and health problems associated with the increase in acidity of precipitation in recent years, Region II, Environmental Protection Agency, the New York State Department of Environmental Conservation, the Cornell University's Water Resources and Marine Sciences Center and Center for Environmental Quality Management are sponsoring this Conference to inform selected environmental agencies, industries, and public interest groups of the phenomenon and current knowledge of the effects.

This Conference was supported in part with funds provided by the Zurn Foundation, Erie, Pennsylvania, and by the U.S. Department of the Interior, Office of Water Research and Technology, pursuant to the Water Resources Research Act of 1964 as amended.

TABLE OF CONTENTS

WELCOME 1
Herbert Posner

INTRODUCTORY REMARKS. 2
Eric Outwater
Ogden R. Reid

ACID PRECIPITATION: A WORLD CONCERN
Keynote Address. 5
Svante Odén

Plenary Session I

ACID PRECIPITATION: OUR UNDERSTANDING OF THE PHENOMENON. . . . 45
Gene E. Likens

ACID PRECIPITATION: OUR UNDERSTANDING OF THE ECOLOGICAL EFFECTS. 76
Carl L. Schofield

HEALTH EFFECTS OF ACID AEROSOLS 88
Jean G. French

Plenary Session II

DISCUSSION SESSION ON THE PHENOMENON. 96
John Hawley, Discussion Leader
James Galloway, Rapporteur

DISCUSSION SESSION ON THE ECOLOGICAL EFFECTS. 99
Jay Jacobson, Discussion Leader
Don Charles, Rapporteur

DISCUSSION SESSION ON HEALTH EFFECTS. 105
Donald Casey, Discussion Leader
Walter Lynn, Rapporteur

PARTICIPANTS. 107

PROGRAM 113

WELCOME

Herbert Posner*

Mr. Posner, in welcoming the participants to the Conference, made special mention of those from out of the country and out of the State. He expressed pleasure that the Conference includes scientists from outside the United States since acid precipitation is an international problem. Mr. Posner also expressed the hope that the approach being taken here to determine the parameters of the problem and possible solutions will become a model to assist decision makers in finding appropriate technological, social and economic solutions to important problems.

He emphasized the difficulty faced by the Legislature and especially the Environmental Conservation Committee in keeping up to date and informed about the multitude of environmental problems, such as Freon and ozone, LNG storage, sludge, carcinogens in drinking water, and acid precipitation. Mr. Posner lauded the competence of the Assembly Scientific Staff in providing the needed technical assistance to the Assembly.

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*Chairman, Environmental Conservation Committee, New York State Assembly, State Capitol, Albany, New York 12224

INTRODUCTORY REMARKS

Eric Outwater*

Mr. Outwater briefly touched on some of the important environmental problems which are of particular concern to EPA and EPA's commitment to solve them. In addition to its pollution abatement and control activities, which involve research, monitoring, standards setting, and enforcement, EPA coordinates and supports research activities by State and local governments, and private and public groups. Mr. Outwater expressed gratification for the cooperation received from the N.Y.S. Department of Environmental Conservation on issues with which the two agencies worked together.

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*Deputy Regional Administrator, Region II, U.S. Environmental Protection Agency.

Ogden R. Reid*

I would like to welcome all of you from different parts of the country and Europe. Dr. Oden, you have helped lead the world in important directions and we're very grateful for the opportunity of having you here.

I judge many of you attended the First International Symposium on Acid Precipitation recently held in Ohio. I've heard brief reports about it, and that the European representation was particularly creative and helpful. My understanding is that in Scandinavia, using lichens as a test for sulfur oxides in the air provides yet another example of the importance to man of every manifestation of nature. I certainly want to thank you for your pioneering effort.

One thing that I think has struck all of us is that our flora, fauna, fish and forests provide early warning of problems. I think that there is some evidence that we are seeing some abnormalities on the leaves of yellow birches; that pine needle lengths have varied in some areas of the western Adirondacks, and certainly the life expectancy of fish in some of the Adirondack lakes is very low. As all of you know, the latter is probably related to the pH content in the lakes. We have found that the pH in some of the lakes has gone from 5 to 3.5 on the pH scale. On this scale, 1 is corrosive acid; 14 is corrosive alkali; 6 to 8 is considered normal and "safe" for humans and animals.

It may be too early to make a judgment as to whether or not this is characteristic of most of the lakes in the Adirondacks. However, in sampling of water from 80 lakes, Schofield (Cornell) found that 35 were

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*Commissioner, N.Y.S. Department of Environmental Conservation

below 6 pH. Of these, 33 were in the western Adirondacks where precipitation is high and the lakes contain less soil and natural minerals or buffering agents, such as lime or alkaline salts.

One of the problems is that the sources of pollutants are difficult to trace and the transport mechanism is not clearly understood. It is believed, however, that sulfur and nitrogen pollutants are coming from industrial smokestacks, primarily in the Midwest and Canada.

The Department plans to initiate an interdisciplinary research program to study these problems. In addition to air sampling to determine the source of acids in the air, it is planned to take water samples from large numbers of lakes in the Adirondacks and analyze their pH levels. We thereby hope to determine the extent of the problem, the effects on health, the environment and the economy, and possible solutions.

There are many other environmental problems which confront us such as the Outer Continental Shelf, the stratosphere, carcinogenic inducing substances, and land use, to name a few. Meetings such as this can be valuable in developing parameters for scientific research.

ACID PRECIPITATION: A WORLD CONCERN

Keynote Address

Svante Odén*

The Atmospheric Chemical Network in Europe

The increasing acidity of air and precipitation in Europe and its consequences to soils, vegetation and surface waters were first presented in a Swedish Governmental Report entitled *Environmental Research* (1967). The basic facts in this report originated from long-term network data regarding the chemistry of air and precipitation in Europe and to some extent of surface waters in Scandinavia. At that time the records extended for almost a 10 year period for certain areas in Europe. When plotting these data for the different elements at individual stations it became evident that certain elements showed either a positive or a negative trend with respect to time. The chemical climate was obviously changing in Europe. In order to study the effect on soils and surface waters (and indirectly on vegetation) a surface water network was set up in Scandinavia in 1961-62. My presentation today will be based mainly on data from these two network systems.

Figure 1 illustrates the network in atmospheric chemistry. Each dot represents a sampling station, where precipitation and air have been sampled on a monthly basis. The major cations and anions have been determined as well as pH and electrical conductivity. The network started

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*Department of Soil Science, Division of Ecochemistry, Agricultural College Uppsala, Sweden.

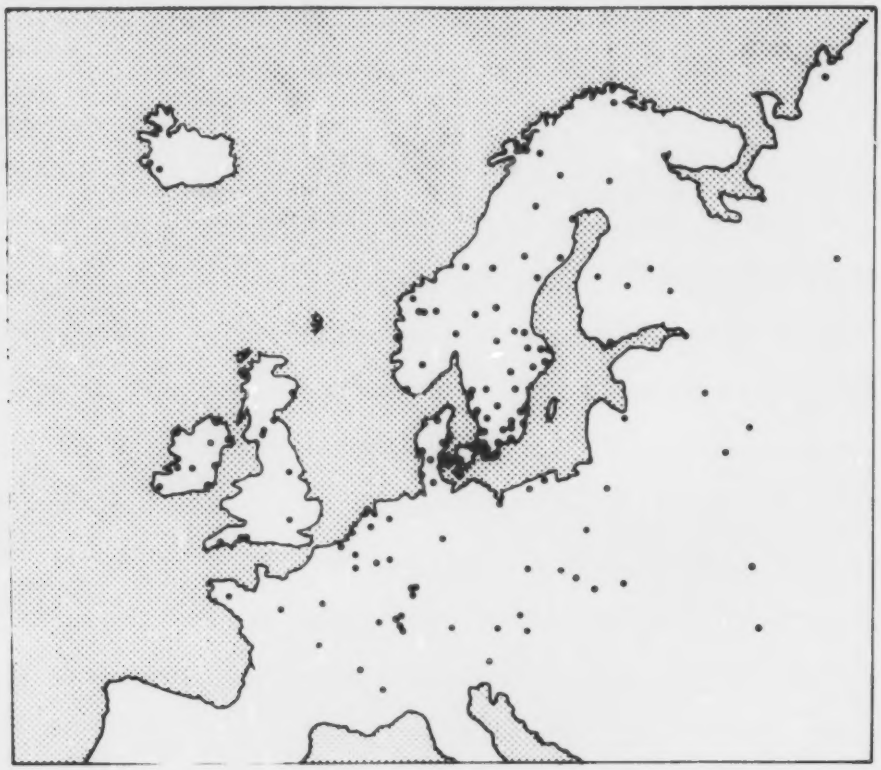


Figure 1. Each dot on the map represents a sampling station for precipitation and air. Part of the network is coordinated by the International Meteorological Institute in Stockholm.

in Sweden in 1948, extended to the rest of Scandinavia in 1952-54, and to the rest of Europe the years thereafter. As part of the program of the geophysical year (1957) a one-year study was made in some countries. The U.S.S.R. started a network over all Asia to the Pacific in 1958, and to my knowledge this network is still operating. The Polish network started in 1964. Data from the last two countries are available for some years. Altogether these data makes it possible to evaluate changes of the chemical climate in Europe at individual stations, and the geographical distribution also. The network density of about 130 stations

(at maximum level) is not dense enough, however, to evaluate the details. The discontinuity between sea and land necessitates a much denser network to give a true picture of the geographical distribution pattern. The U.S. Continent is more homogeneous in this respect and the widespread network that has existed now and then seems appropriate for mapping atmospheric chemical constituents. The present drawback is the lack of consistency with time.

Figure 2 illustrates the position and the intensity of the water quality network in Sweden. In Finland and Norway similar networks are at work. In the beginning the Swedish network operated with a limited number of determinations but since 1965, eighteen elements or other determinations have been made on every monthly sample. Since the water flow is also determined, the discharge can be computed for every element. By comparing the atmospheric fallout with the river discharge, the effect of changes in the chemical climate can be determined. The influence of farming, water pollution or other widespread or intense activities, however, may distort such computations.

Figure 3 shows the time records of the fallout of nitrate (NO_3) and ammonia (NH_4) from some stations of the European network. A more or less continuous increase with time takes place, and the rate of this increase is more pronounced at stations closer to the center of Europe. This is therefore likely to be the source center for NO_3 and NH_4 in the atmosphere. Data from the individual stations vary to some extent from year to year, reflecting variations in both source and sink conditions and large-scale meteorological interferences. Occasionally very high figures may appear (cf NH_4-N at Å̊s in 1967 and 1972). Other stations show a wave-pattern

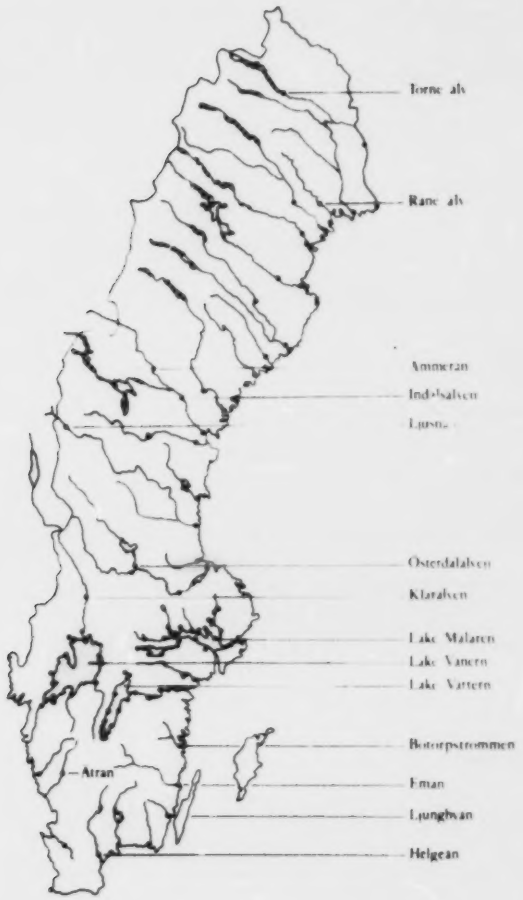


Figure 2. The major lakes and rivers in Sweden. The dots show the location of the sampling stations. Most of the network is administrated by the Limnological Laboratory, Uppsala, Environmental Protection Board of Sweden.

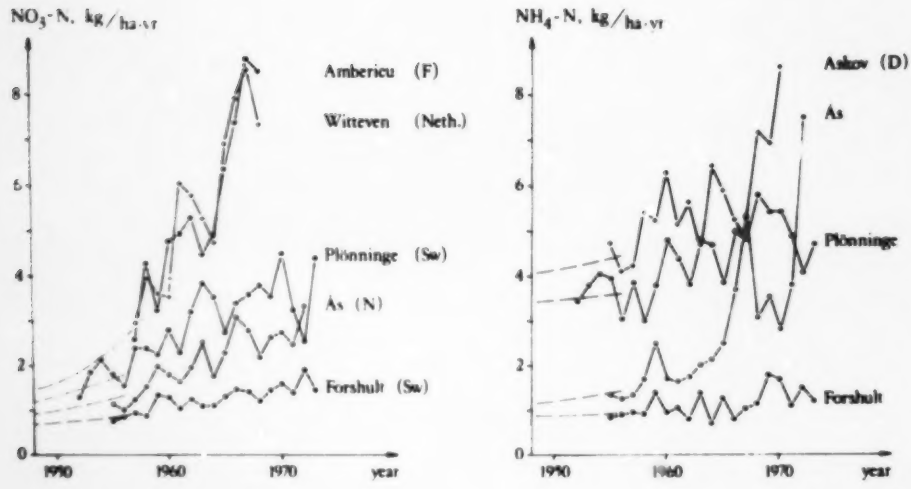


Figure 3. Time records of the wet fallout of nitrate and ammonia at some stations within the European network. The stations vary latitudinally from 60 Degr. N (Ås and Forshult) to 46 Degr. N (Amberieu).

with simultaneous increasing or decreasing values (cf NO_3-N at Amberieu and Witteven). This yearly variation occurs for almost every element and points out the necessity of long-term records in order to determine any trends in the data.

Nitrate in precipitation is basically man made. The increase in Central Europe is very pronounced. In the middle of the nineteen fifties the fallout was less than 2 kg/ha·year. Prior to 1950 the fallout of NO_3-N did not vary too much among different stations in Europe. The baseline figure for all stations was likely to be around 1 kg/ha·year or less. The very pronounced increase of NO_3-N is due to the large emissions of NO_x from various industries, high temperature engines and oil-based power plans. In the atmosphere NO_x is oxidized to nitric acid. This compound consequently forms part of the atmospheric acidity.

The station records for NH_4-N indicate somewhat different figures. The increase with time is not so pronounced and the background values for the different stations seem to be fairly well separated, at least around 1950. Going further back in time these values may narrow, but it is very unlikely that they will coincide for the different stations in Europe. The reason for this is that NH_3 is liberated from soils and eutrophicated surface waters, giving rise to diffuse and local source areas. Such are the intensely farmed (including cattle raising) parts of Europe and the shelf areas of the North Sea. The increase of NH_4-N during the last decades reflects, too, the influence by man but differently from NO_3-N. Farming intensity has increased during this time (primarily because of the use of fertilizers) and it is well known that the eutrophic level of the North Sea as well as lakes and rivers in Europe has become higher. Consequently the diffuse emissions of NH_3 has increased.

The wet fallout of total nitrogen forms a distinct pattern over Europe. In 1958-59 (Figure 4) three areas with more than 8 kg/ha·year appeared, and the fallout was reduced extending outwards from the Center of Europe. In Northern Scandinavia the value was less than 1 kg/ha·year. Ten years later there was an overall increase of the fallout by a factor of 2. The concentric pattern, however, still exists. The data from Polen have been extrapolated for the years 1968-69.

NH_4-N takes part in the acidity problem in at least two ways. NH_3 neutralizes acids formed when SO_2 is oxidized. This leads to enhanced oxidation rate of SO_2 and consequently of the final oxidation product, which is sulphuric acid. The increased emissions of NH_3 promotes the formation of acids within a narrowing area. On the other hand, the acids

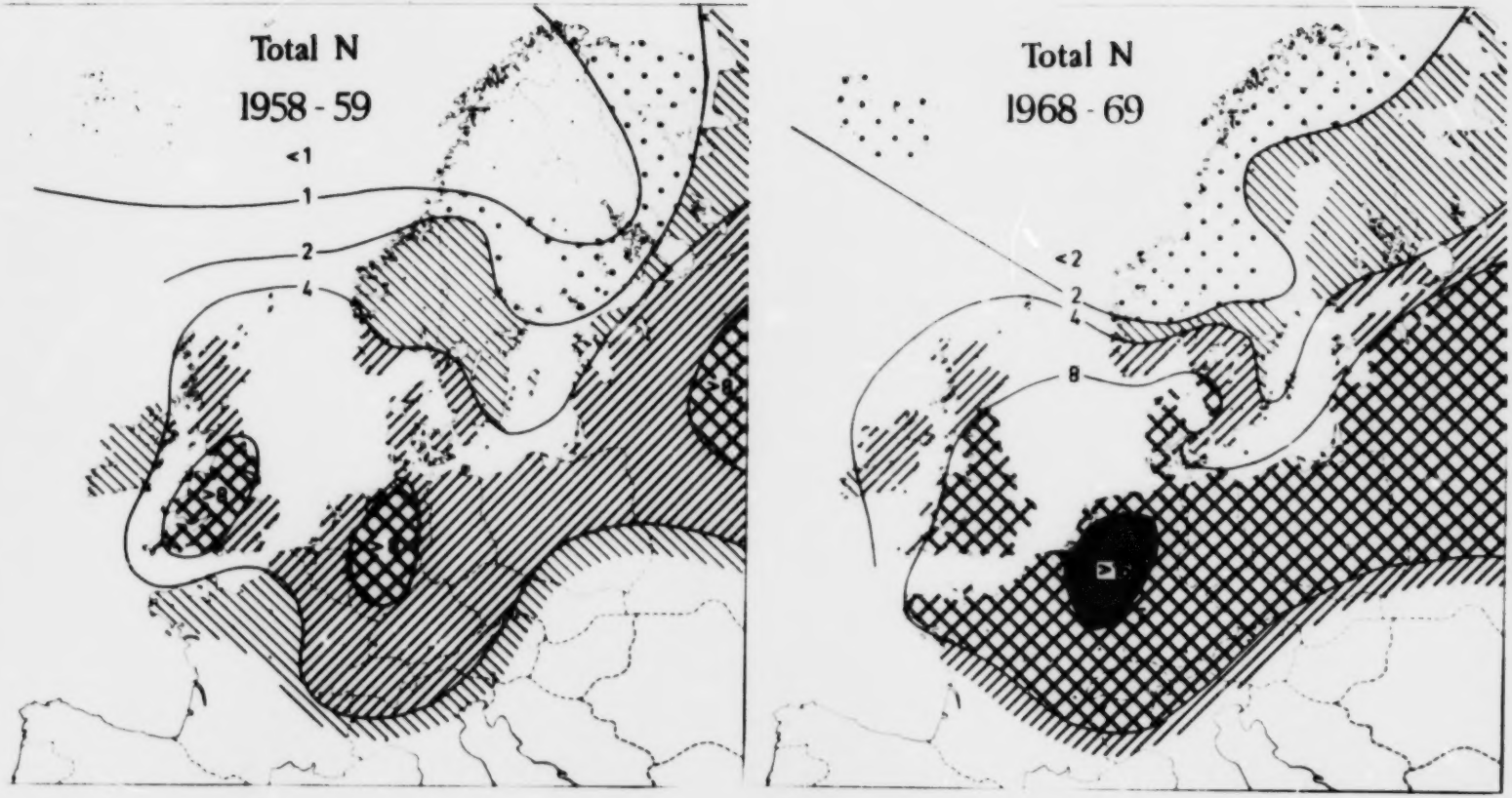


Figure 4. The maps show the geographical distribution of the wet fallout of total nitrogen (NO_3-N and NH_4-N) for the averaged period 1958-59 in comparison with 1968-69. Figures are given in kg/ha·year.

formed will be more or less neutralized from an atmospheric chemical point of view. The acidifying effect of neutral or acid ammonium sulfate on reservoirs like soils and surface waters, however, will be equally strong as that of the pure acid, since the ammonia part will be resorbed by the plants. This forms part of the process I have called "biological acidification."

Particles of $(NH_4)_2\ SO_4$ or $NH_4H\ SO_4$ formed in the atmosphere are very small and consequently widespread. The net effect of counteracting processes of NH_3 can not be computed at present. The rapid increase of the acidity of lakes and rivers in Scandinavia indicates, however, that both the increase of the production of acids and the spreading of these acids has enhanced the acidification of remote areas in Europe.

Other elements than NO_3-N and NH_4-N show time trends. Thus S and H increases with time as will be discussed later. Cations like Ca, Mg and K appear very irregularly in the data. At some stations they increase with time; at others they decrease. This state of contrast seems to be related to local industrial activities giving rise to increasing or decreasing emissions. The overall picture for Europe is a slight increase in the sum of the above elements.

The elements Na and Cl form a very distinct geographical pattern for Europe with high fallout figures along the marine shore lines. The picture is equivalent for the United States and the relation of these elements to marine salts is well known. There is no trend in the data of these elements, but there may be a periodic variation with a time period of 8 years.

The Acidity of Precipitation

pH in precipitation has decreased considerably at almost every station in Europe. Figure 5 gives an example of the monthly values from Tystofte

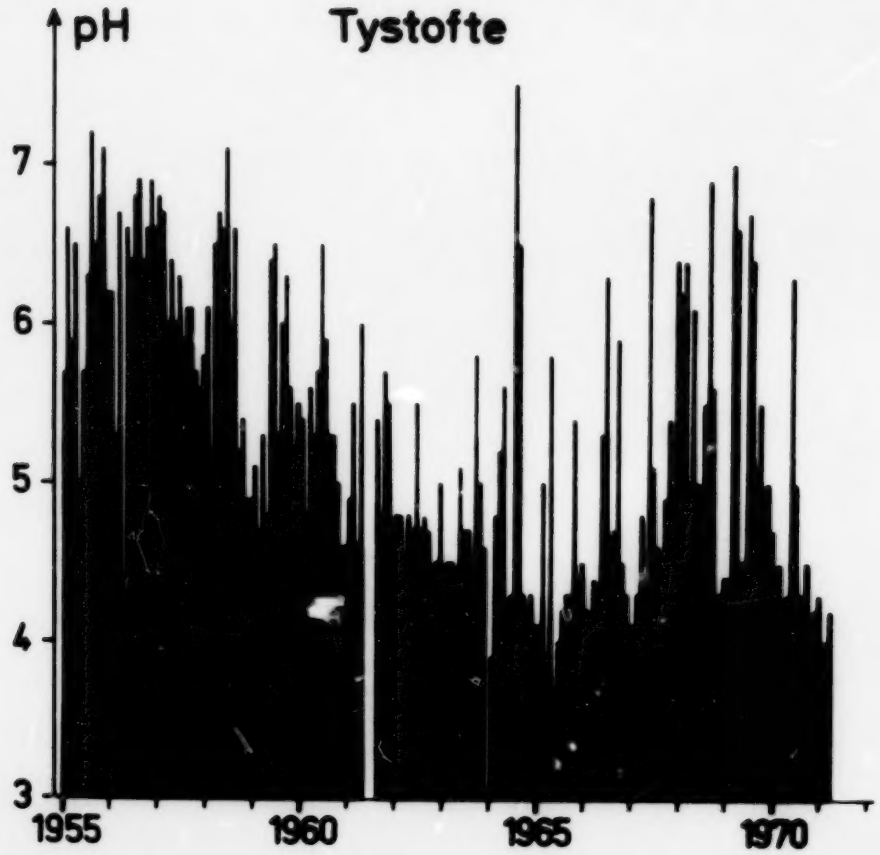


Figure 5. Monthly pH-values from the station Tystofte in Denmark from 1955 - 1971. The station is still in operation but data are not yet available.

in Denmark. The Figure illustrates three phenomena rather common in this type of data:

1. The occasional occurrence of higher to much higher pH values in relation to the general bulk of data. They appear mostly in summer time and are likely to be due to local deposition of alkaline dust. The lack of co-variance between nearby stations excludes a more largescale effect. In general, summer values are higher. This can be seen for the years 1958, 59, 60, 64, 65, 66 and 69.

2. A long-term periodicity seems to appear at this station. The length of the period is approximately 12 years. The correlation with nearby stations is fairly low, which indicates that the variation at Tystofte is local or less than the grid of the network. For other stations a co-variance may appear for certain years (cf Figure 6).

3. Generalized for the period, a negative trend takes place at Tystofte. The pH-values drop from approximately 6 to 4. The same takes place at almost every place in Europe. Due to long-term changes of local or regional character, the regression line for pH with time is not so easy to determine.

The large variation in the data on a monthly basis is somewhat reduced when yearly average values are computed. Examples from 6 stations are given in Figure 6. The sequence of yearly data show, nevertheless, a large variation, which makes it difficult to establish the trend for the period. The solid regression line for each station was drawn (by eye) in 1970. The additional data show that such trends are sometimes not always justified. The trend at Flahult and Plönninge is overestimated, at Smedby underestimated. For the other stations the trends are fairly correct. A straightline relationship means that the acidity has increased exponentially from 1955 to 1974. This is not likely to take place forever, and the most probable trends are curves tending to a limit value of pH 4 or below. In all circumstances the data in Figure 6 illustrates the difficulty to evaluate the atmospheric chemical data. As yet there is, to my knowledge, no method to reduce the variation between years. This ought to be possible, however, since there must be some kind of physical reality in the co-variance between stations. As shown, the curves for Kise and Ås are very similar. For long periods this is also the case for Flahult, Plönninge and Smedby.

The geographical distribution of the yearly mean pH-values of the precipitation are shown in Figure 7. In 1956 a center of acidity (pH 5.0-4.5) appeared over southeastern England, North of France and the Benelux

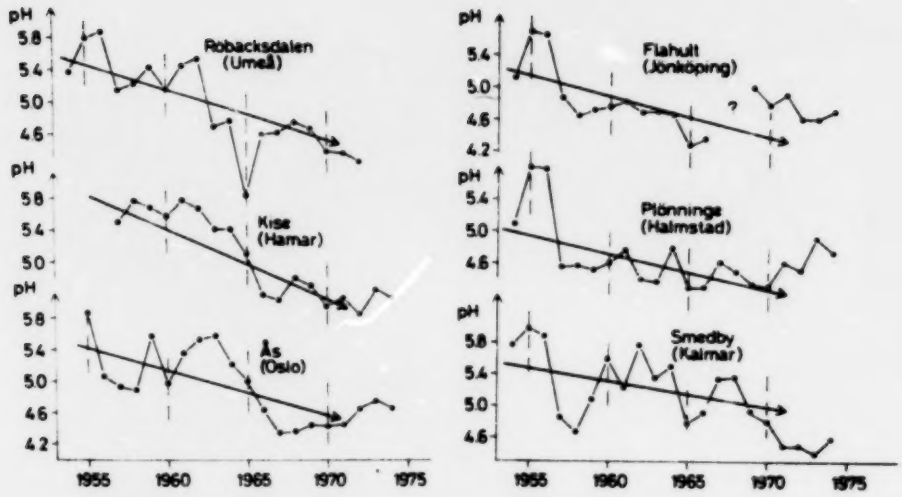


Figure 6. Yearly average pH-values from 2 station in Norway and 4 in Sweden. The straight trend lines were drawn in 1970. Note the effect of additional data.

countries. Three years later the central area had become more acid (by 0.5 pH-units). The acidity is reduced outwards. The data from the U.S.S.R. makes it possible to show that the European acidification was regional in 1959 and mainly isolated from the rest of the Continent. There is only a tendency for an impact on northeastern European countries.

In 1961 and 1966 the situation worsened. In small areas (Benelux countries) the yearly average pH-values were below pH 4 and areas interfered by pH 4.5 - 4.0 were very large in 1966. The maps indicate that the acidity was spreading to the east with the prevailing winds. On the other hand, it can not be excluded that a second acidity center in U.S.S.R. and the eastern European countries also has been enlarged and intensified, forming a combined area of increased acidity with that of central Europe.

Maps have not been prepared for the years after 1968. This is partly due to lack of data from some countries and partly to the fact that the

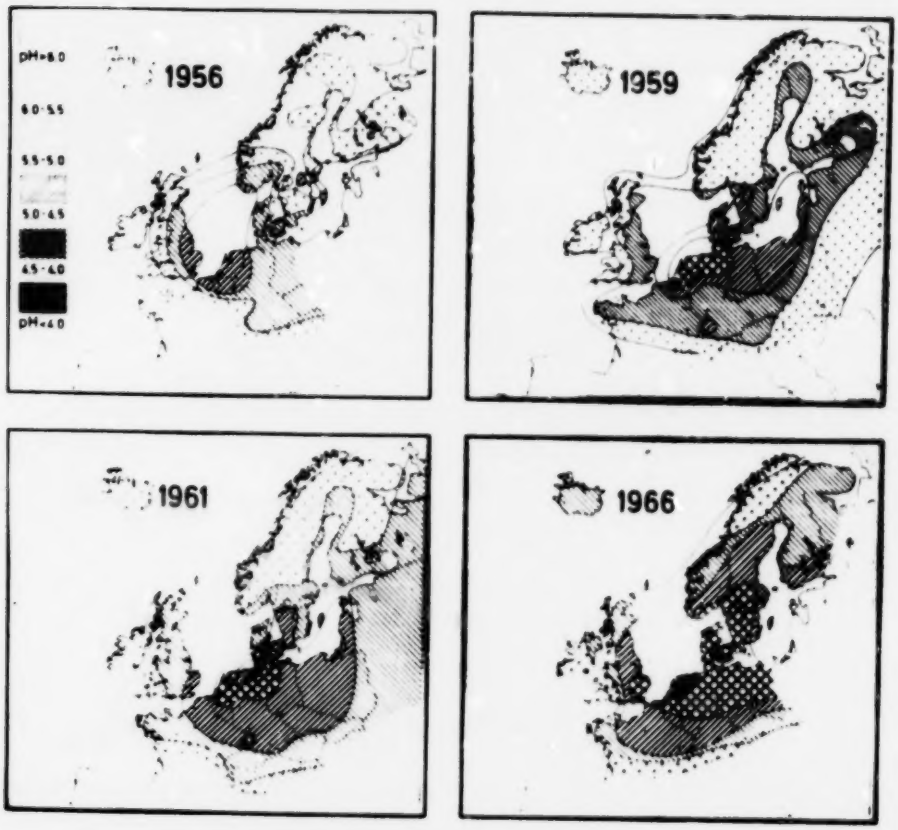


Figure 7. pH-maps for Europe for four years. Isolines differ by .5 pH-units. The maps are based on the yearly average of 12 monthly samples.

yearly average pH-values are not properly related to the fallout of acids or acid-forming substances. If, for example, the precipitation is sampled for a whole year, the pH-values would be roughly .2 pH-units lower than those given in Figure 6 and 7. This is a consequence of the fact that a single monthly sample with a high pH-value may increase the yearly average figure considerably but does not contribute to the acidity. The long-term station records (cf Figure 6) indicate, however, that the acidity is still increasing in Europe.

There is no doubt that sulfur forms a major but complex part of the acidity of precipitation. At almost every station the sulfur content is steadily increasing while pH is decreasing. Four examples are given in Figure 8 to illustrate this relationship. A negative correlation is obvious, but in the details the correlation is not too good. Changes in the fall-out of bases like NH_3, Ca, Mg and K as well as acids like NO_3 will also contribute to the acidity or the alkalinity of a sample. Actually, when all ions are taken into account, the pH-values can be computed from the balance of ions. This has been successfully done by the International Meteorological Institute (Granat, 1972) and at Cornell (Cogbill et al., 1974).

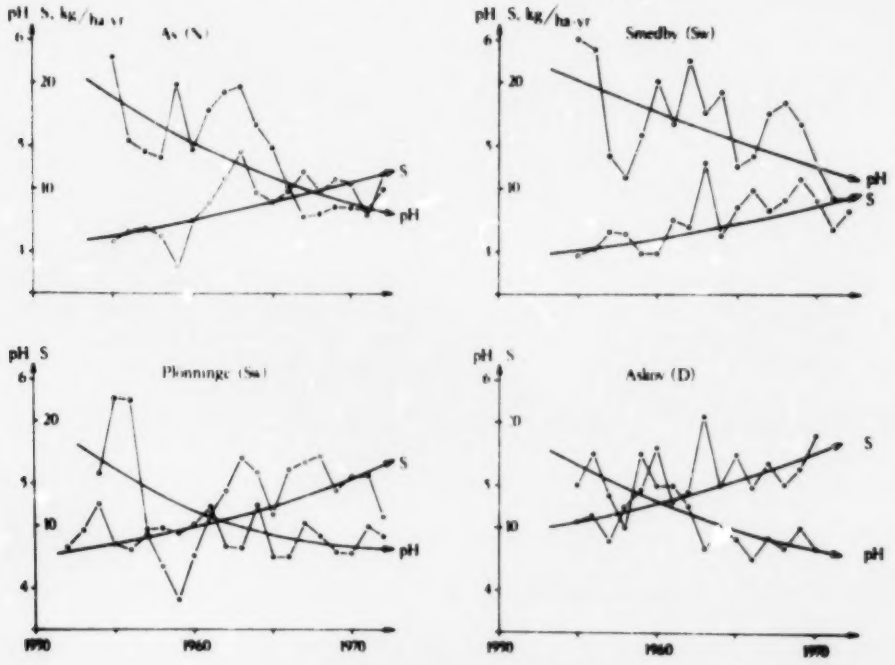


Figure 8. Sulfur and pH year by year at four stations in Scandinavia.

When the fallout of sulfur is plotted year by year, the pattern is very irregular. Some years the fallout is markedly higher in central Europe and U.S.S.R.; other years this pattern disappears more or less. The fallout of sulfur is obviously very sensitive to other factors than the amount of emission. This has actually increased by 2 to 5% during the last 15 years, but there is no smooth response in the fallout. There are a multitude of causes to this. Some of these are listed below:

1. Photo-chemical oxidation of SO_2 with or without the influence of
2. the concentration of ozone or
3. the occurrence of catalytic dust particles, or
4. the amount of NH_3 in the air, which dissolves in acid water droplets. Furthermore,
5. the products formed will have different life times in the atmosphere, and consequently the spreading effect will be different. Unlike other elements,
6. the mixing of different air-masses may enhance or retard reactions according to 3 and 4, and the spreading effect according to 5. Finally,
7. sulfur takes part in exchange processes with soils, vegetation and surface waters. Small changes in this exchange may influence strongly the fallout and consequently the spreading of sulfur.

As yet, the effect of the complex sulfur chemistry has not been worked out taking all these factors into account. Conflicting statements are quite common. When the sulfur-acidity problem was first presented, various objections were presented. Among others it was stated that the lifetime of SO_2 was only a couple of hours. Consequently the emissions of SO_2 from Great Britain or central Europe could not reach Scandinavia, since sulfuric acid is very hygroscopic and falls out very rapidly after its formation. Erronously evaluated cruise-data between Sweden and

Great Britain was used to support this view. A second statement was that SO_2 emitted in Great Britain is totally absorbed by the British grasslands. However, the final sink for sulfur has not been presented. Vegetation and soil humus is only a temporary sink for sulfur, and sulfur, absorbed by plants, has to show up somewhere else, e.g., in surface waters. This is not known to take place in Great Britain.

The emission of sulfur varies considerably between different countries in Europe. The figures below are computed from the Swedish Case Study: *Air pollution across national boundaries. The impact on the environment of sulfur in air and precipitation*, which was presented at the U.N. Conference on the Human Environment in 1972.

Emissions of sulfur from some countries in Europe in 1965

The figures are given in kg S/ha·year

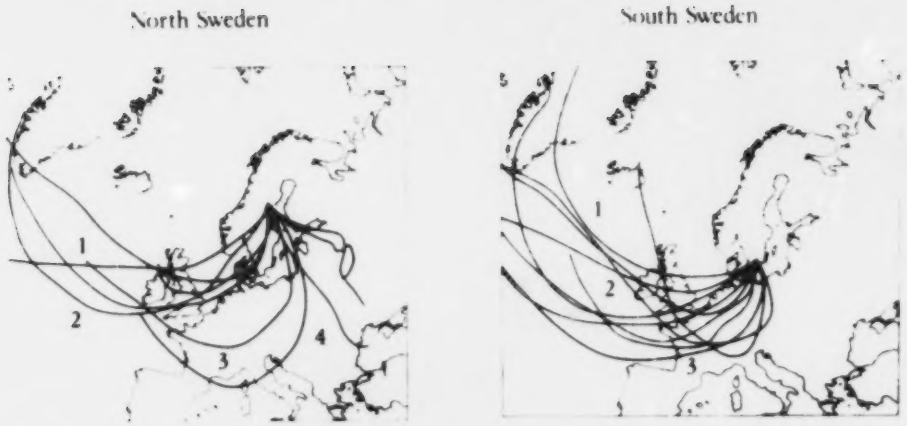
Norway	2.5	France	20
Sweden	6.7	U.K.	131
Denmark	30	Holland	152
W. Germany	65		

These figures show a very large variation among the countries. High figures are likely to indicate that the atmospheric export is high, too. This will especially be the case when a low-level country is situated close to a high-level country. A considerable import of sulfur to the north Scandinavian countries from the United Kingdom and central Europe will thus take place. This is evident from the sulfur content in Swedish rivers. Only part of the discharge of sulfur can be accounted for by the emissions within Sweden. Other countries like West Germany, North France and Holland will just exchange their emission products. The geographical distribution

of regions with intense emissions of sulfur along with meteorological conditions forms a complicated pattern which not yet has been evaluated quantitatively. An OECD-study has been undertaken in northern Europe in an effort to tackle these interactions.

In 1961-62, I made a study of the chemistry of individual rain storms and, simultaneously, determinations of the wind trajectories. Applied to the present problem some results are given in Figure 9. The curves on the maps show the trajectories three days prior to intense precipitation in North and South Sweden respectively. They include all occasions with precipitation during two months. The air masses are obviously passing different parts of emission areas in Europe, and will consequently be polluted with respect to that. When precipitation is formed, the different pollutants will fall out. The least contaminated air (1) leads to a precipitation with highest pH-value and lowest figures of S and Tot-N. At trajectories 3 and 4 the pH drops and S and Tot-N increases substantially. The situation for Cl is reversed, which is logical due to the ocean as the main source for Cl. Dry and wet fallout along the trajectories reduces the content.

The trajectories in Figure 9 show that the winds at precipitation periods are mainly from west to south with respect to Scandinavia. At dry conditions this is not equally well pronounced. Figure 10 shows (by dots) the endpoints 24 and 60 hours respectively from a starting point denoted by a circle. The spread of the endpoints is almost circular. The mean position of all points (denoted by a cross) shows that a slight mean wind to the east takes place. This is in accordance with the maps for total-N and for pH.



Trajectories at rain	pH	S	Tot-N	Cl
1. N Great Britain and Denmark	5.2	0.8	0.2	2.3
2. S Great Britain and Benelux	4.9	1.1	0.3	1.1
3 & 4. Central and E Europe	4.7	2.6	0.7	0.6

Figure 9. Wind trajectories to Sweden at all occasions of general precipitation. The chemistry of the precipitation reflects the emission situation in Europe. Sampling period: October and November 1962

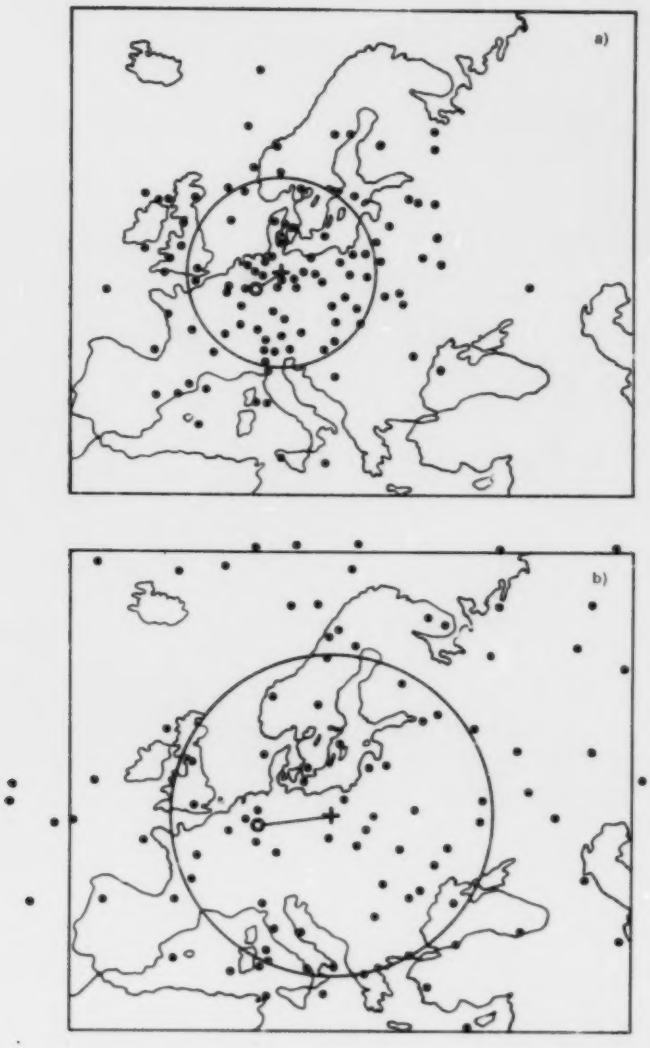


Figure 10. End points of trajectories at a height of 1.5 km from a point (marked by a circle) in Northern Central Europe for (a) 24 hours and (b) 60 hours calculated every third day for a period of about one year. Fifty percent of the points are to be found within the circles which are centered around the mean position of all points (marked with a cross). From Swedens Case Study.

The last two slides show clearly that the possibility for interactions between different countries in Europe through the movements of air masses is fairly large. There is no agreement, however, to the quantitative aspects and neither to effects. As long as this state of matter persists, reduction of emissions is not likely to be made.

Several studies have been made in Sweden and elsewhere to determine the spreading distance from an isolated city or a point source like smelters, power plants or paper mills. Theoretically this distance is indefinite. However, measurements of this distance are limited not only to the sensitivity of instruments but also due to the difficulties of defining a proper base-line or background value. This is especially the case for elements which take part in geochemical cycling, as, e.g., sulfur. The high "noise level" and the more periodic fluctuations leads to an underestimation of spreading distances. The spreading tail will thus be incorporated in the background. At a place remote from cities and industries many such tails may add up anonymously, leading to a change in the chemical climate. This is what has taken place in Europe and large parts of North America. A dome of smoke particles and chemical constituents covers these areas more or less constantly. The local improvements by means of tall stacks has led to an extension of this pollution dome. Figure 11 shows what is visible in this respect: The emission of soot from cities and industries along with soil erosion from deserted areas.

The amount of acids in a sample of precipitation is uniquely defined by the pH-value at unbuffered conditions. When weak acids appear, the buffer capacity of these acids has to be taken into account. Some reports from the U.S. claim that weak acids make up a major part of the acids in

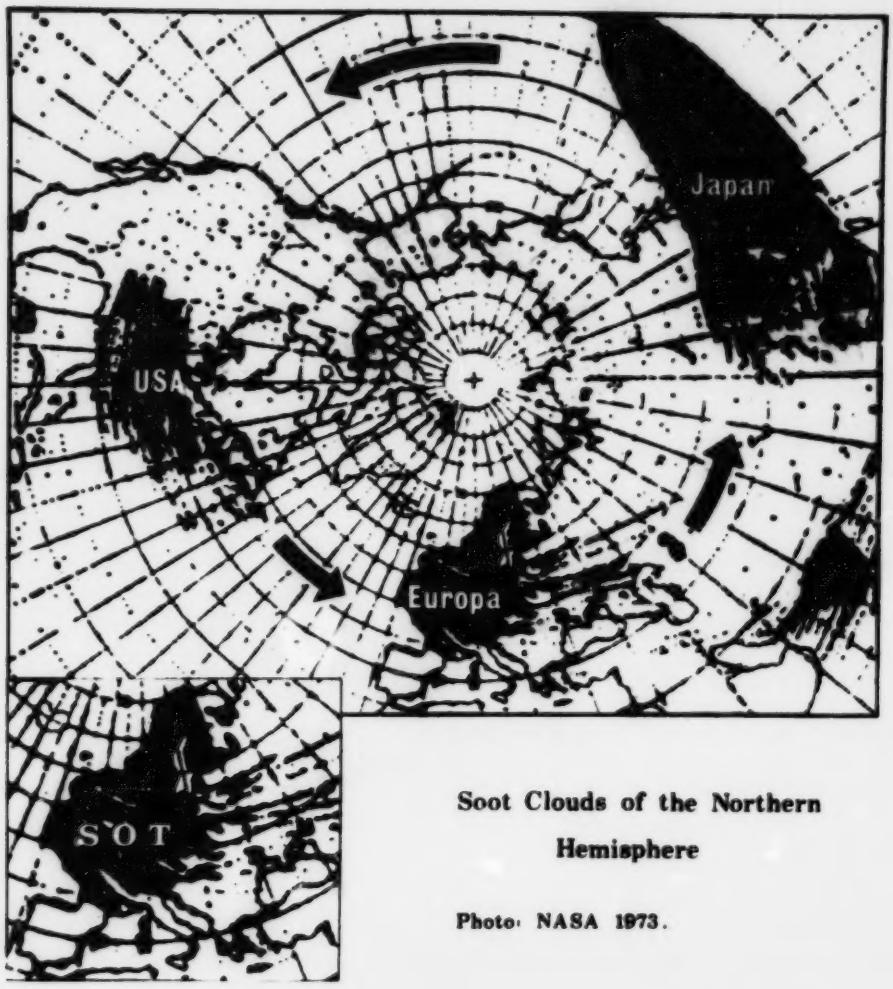


Figure 11. The black parts on this satellite picture denote areas with reduced air visibility due to soot and dust.

precipitation. This is not the case in Europe. Weak acids like acetic acid or other organic acids or salts of iron or aluminum may appear occasionally but their quantitative part in relation to the total acidity is only a few percent. The differences between U.S. and Europe in this respect can not be explained at present. Ongoing intercalibration between laboratories in the U.S. may give the answer very soon.

Another concept with respect to the amount of acids has been proposed and even applied, e.g. in the Swedish Case Study. It has been called "excess acids" and is computed by subtracting the sum of alkalinity for those months with pH > 5.6 from the sum of acids in monthly samples with pH < 5.6. pH 5.6 has been chosen because it is the pH-value obtained when distilled water is in equilibrium with the CO_2 of the air. However, local contamination by dust, lime, ashes, etc. takes place at the sampling station now and then (cf. Figure 5) and leads normally to high alkalinity values. Such a monthly value may therefore be correct for the immediate place of the sampling station but may be incorrect for a place 100 meters away. The almost non-existent correlation between stations for months with high pH-values shows that such values are not representative in a regional sense. The concept of excess acids leads consequently to an underestimation of the fallout of acids.

Another point has to be stressed. The concept of the atmospheric acidity may be defined chemically in relation to pH 7.0 or pH 5.6 or any other point of reference. Such definitions, however, do not account for the acid (or alkaline) effect that will take place, when precipitation is added to other systems like soils, waters, vegetation, metals, buildings, etc. As an example, a precipitation of pH 6.0 is chemically slightly acid with respect to the neutral point of pH 7.0, fairly acid with respect to ocean water of pH 7.8 or a wall of concrete of pH 8.5, but it is alkaline with respect to a farm soil of pH 5.0. The low pH-values at present in part of the U.S. and Europe (pH 4.0 - 4.5) are still alkaline with respect to a peat bog with pH-values normally below

4.0. Consequently, the acidity of precipitation and the amount of acids in precipitation can only be defined in relation to something outside the sample, and these quantities must therefore be given different values. Only changes (in time or between places) are chemically definable from intrinsic properties of the precipitation sample(s).

Changes in the Chemistry of Surface Waters

Changes in the acidity of air (dry fallout) and precipitation (wet fallout) will have an impact on natural reservoirs as well as technical systems. Through the water quality network and adjacent studies of soils and surface waters a substantial amount of data have now accumulated to establish various effects of this impact. For the most part, my original presentation of these effects in 1968 have been verified by subsequent data (Oden, 1968).

Figure 12 shows the monthly pH-values from three of the fifteen sampling stations, which started in 1965. Their locations are given in Figure 2. These records (along with the other 12) show (1) random variations, (2) seasonal variations, (3) yearly variations, (4) time trends and (5) a singular discontinuity. Some of these points will be discussed in some detail.

A seasonal reduction of the pH-values takes place almost every spring. The effect is most pronounced in small watersheds, at high altitudes and in northern latitudes. In complicated river basins with a mixture of waters of different age and chemical quality at the point of sampling, this effect vanishes almost totally. Sometimes the drop in pH occurred simultaneously with other changes like increasing color and the content of oxidizable material as measured by the consumption of $KMnO_4$ (cf. Figure 13).

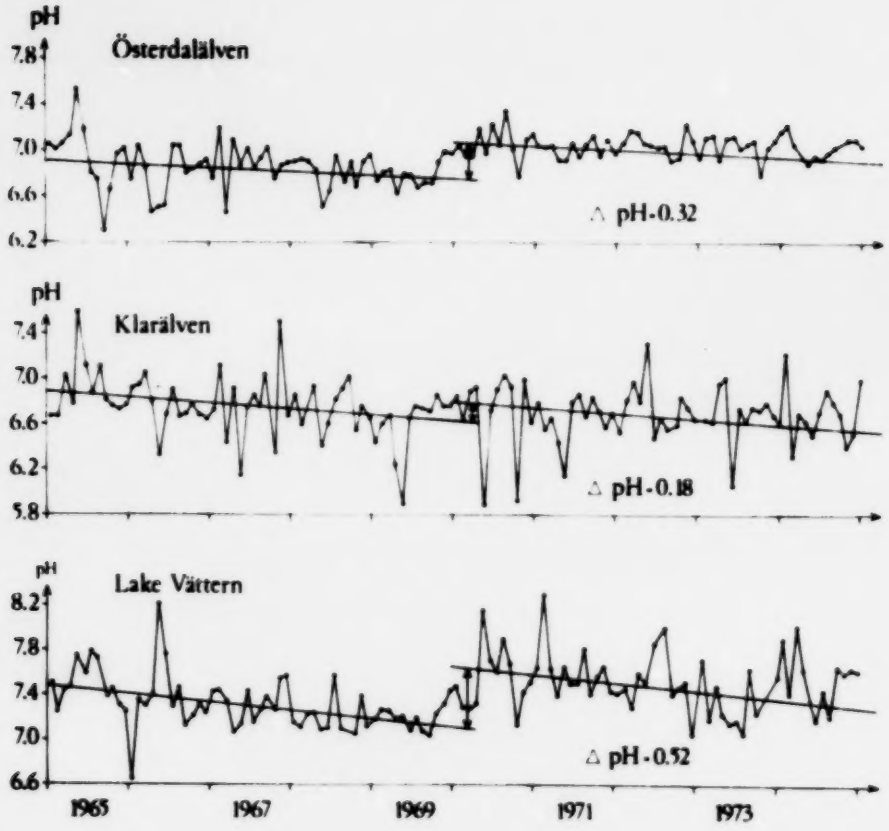


Figure 12. pH-records from 3 sampling stations of the Swedish water quality network during 1965 to 1974. Δ pH refers to the discontinuity denoted by an arrow in the beginning of 1970.

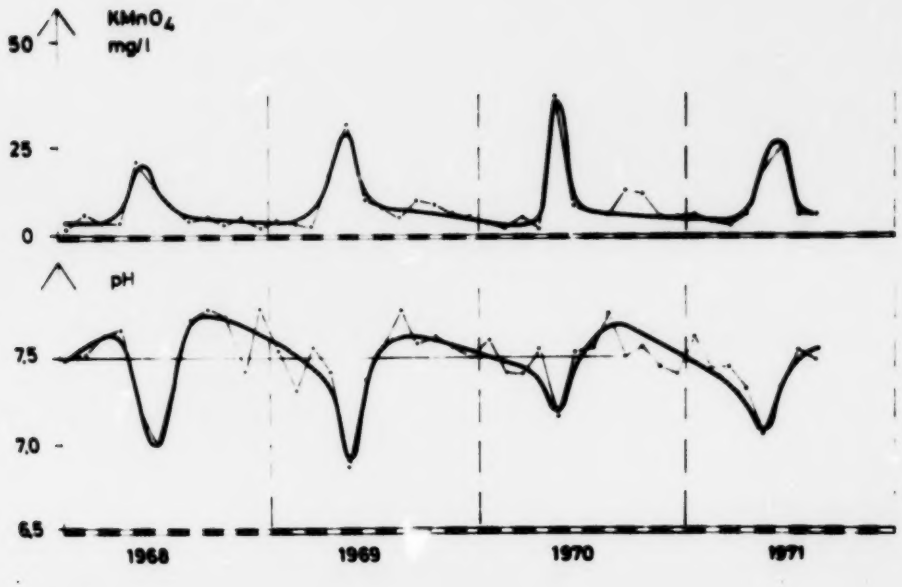


Figure 13. Records of pH and the consumption of $KMnO_4$ from the sampling station at river Ljusnan. The station is localized in Figure 2.

This effect proved to be related to the melting of the snow cover. In the first phase of the melting period most ions separate from the package of snow. The meltwater is salty and much more acid than the bulk of snow and will drain on top or in the upper layer of the otherwise frozen soil. A rapid flow to the tributaries of the river gives rise to drastic changes in the chemistry of the river water. Such changes may have a profound influence on fish life as a kind of shock effect.

During the second phase of the snow melting almost distilled water infiltrates into the soil. If the ground water reservoir is filled at that time the equivalent amount of more or less alkaline ground water is extruded into the surface waters. pH is then rapidly restored.

This model has been applied and verified by others in Scandinavia. The effect on thermally stratified lakes has been shown to be of special interest.

The discontinuity in the pH-records in 1970, denoted by an arrow in Figure 12, is also related to snow. The storage of snow was especially large during the winter of 1969-70. The soil, however, was almost unfrozen that winter and at snow melting most of the meltwater infiltrated into the soil leading to the alkaline ground water effect discussed previously. The Δ pH at the point of discontinuity is well related to the amount of calcareous materials in soils and the bedrock within the different river basins. Where calcareous materials do not exist the pH-discontinuity is not noticable.

The pH-trends in all Swedish rivers investigated since 1965 (some from 1963) are all negative. The regression lines seem to be straight within the investigated period, and the discontinuity in 1970 apparently does not lead to a change in the slope. If the slopes are extended to pH 5.5, which is supposed to be a biologically critical pH-value, a "lifetime of health" is obtained. On the average, 60% of the investigated rivers in Sweden will reach this critical point in 40 years, and as much as 90% in 80 years. Each discontinuity will extend these ages by 4 years on the average. The frequency of such jumps, however, is not known.

In 1965 and 1970 we made a synoptic water quality study of Scandinavian surface waters by roughly a 1000-point network. pH showed up to form several regions with lower pH-values than the surrounding areas. Such regions were southwestern Norway, the westerly part of Sweden and some areas in the interior of middle and southern Sweden. The reduction in pH in these regions is most likely a consequence of the

increasing acidity in Europe along with soil conditions of low buffering or neutralizing capacity.

Natural waters are normally buffered by soluble substances (PO_4, organic acids, amino acids etc.), colloidal organic matter (humus, seston) and bicarbonate. A set of buffering curves from stations of the Swedish water quality network is shown in Figure 14. The rivers SE, SF and SL have obviously low buffering capacity and are consequently sensitive to additions of acids. The shape of the curves makes it clear that all waters are very pH-sensitive in the range of pH 4.5 - 6.5. Small additions of acids at a pH of 6.5 may thus cause a rapid drop to pH 4.5. Above pH 6.5 the waters may be highly pH-stable due to bicarbonate (cf. SA and SB in Figure 14).

At present the content of bicarbonate steadily decreases in Swedish lakes and rivers. As such this has no direct biological consequences but it indicates the chemical changes that occur. The waters, however, tend to be more liable to rapid pH-changes, which is known to interfere with fish life. The reduction of bicarbonate is due to the addition of strong acids within the watershed area. The only acid of any importance in this respect is sulfuric acid or its salt ammonium sulfate. The ratio HCO_3/SO_4 is consequently a sensitive index (besides pH) of the continuing acidification of natural waters. Four examples are given in Figure 15. All rivers show a continuous decrease in this ratio. The slope is steepest in rivers in the south and west of Sweden, which is in accordance with the atmospheric fallout of acids. When this ratio is zero, bicarbonate has disappeared. pH is then around 5.5, i.e., the pH-value previously discussed as a critical one. When the slopes are extended to its zero

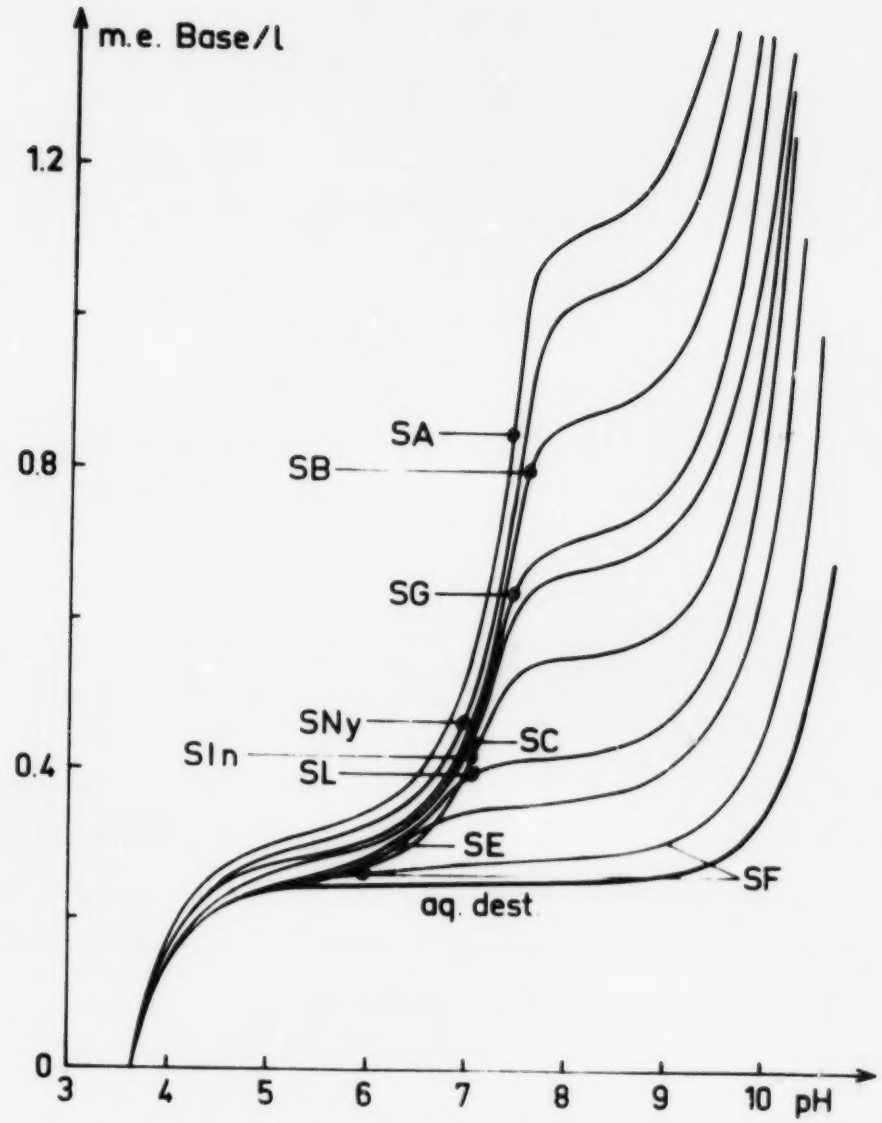


Figure 14. Buffering curves of waters from the Swedish water quality network. The dot on each curve denotes the pH-value at the time of sampling.

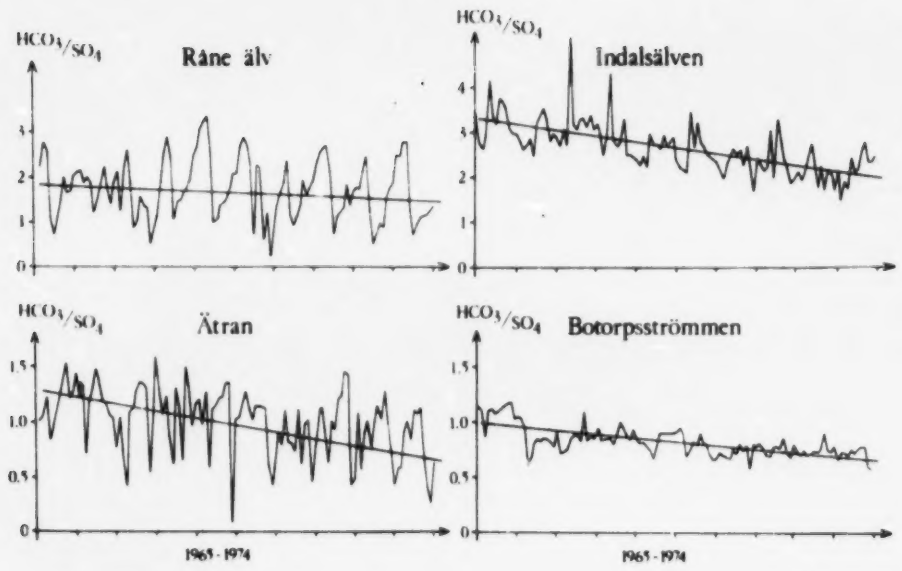


Figure 15. The ratio of bicarbonate to sulfate on an equivalent basis for four rivers of the Swedish water quality network. For location of the sampling stations, see Figure 2.

value, figures for the lifetime of a healthy state of the rivers will be obtained. Such computations give figures which are almost identical with those based on the pH-trends (cf. Figure 12).

The chemical changes in Swedish river waters, illutrated by our data from 1965 to 1974, started, of course, much earlier. This can be illustrated by the relationship between Ca and HCO_3 from three different periods. Each line in Figure 16 represents the regression line for a large number of data from lakes and rivers. As can be seen there is a gradual increase in the slope with time. The discharge of a given amount of Ca will consequently take place with successively lesser and lesser amounts of HCO_3. This is only possible if HCO_3 is exchanged by another

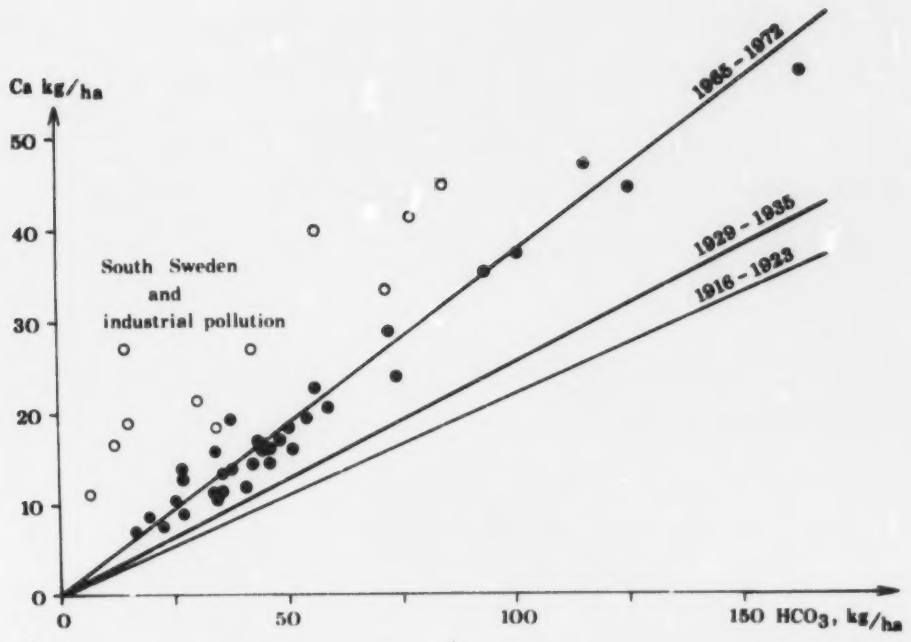


Figure 16. The discharge of Ca and HCO_3 by Swedish rivers at different time intervals. The circles refer to rivers in South Sweden and those polluted by calcium sulfate.

anion, e.g., like sulfate. The figures below show that the discharge of sulfate by Swedish rivers actually has increased considerably since the beginning of this century.

DISCHARGE OF SO_4—S, KG/HA·YEAR

REGION		1909 - 1923	1965 - 1972
NORTH SWEDEN,	> 65°N	2.3	6.3
CENTRAL SWEDEN,	60°N - 65°N	4.4	9.1
SOUTH SWEDEN,	< 60°N	10.3	21.0
SKÅNE - BLEKINGE		12.5	31.0

The discharges of sulfate were more than twice as high at present. When only the anthropogenic part of sulfur is taken into account the increase is three to five times over the period. In the southeast part of Sweden (Skåne - Blekinge) the increase of anthropogenic sulfur is about 20 kg S/ha·year within a period of 50 years. In the form of sulfuric acid, the total load for the period has thus amounted to 1500 kg per ha.

The Impact of Acids on Soils

The chemical conditions in lakes and rivers reflect in a more or less complicated way reactions and changes in the soil system and occasionally in the bedrock. When the lake area is small in relation to the drainage area, neither sink mechanisms in the bottom sediments nor the effect of precipitation on top of the surface water has to be taken into account. In Sweden 80 to 95% of the water in lakes and rivers is actually a mixture of soil water and groundwater.

As a model, the relationship between precipitation (and dry fallout), infiltration, groundwater runoff, surface water runoff and the mixing of different water categories is illustrated in Figure 17. At the soil surface and the zone of infiltration a multitude of reactions will take place.

When strong acids or acid-forming substances are brought to the soil the following reactions will take place. An increase of the acidity of the soil solution will be a primary effect (1). However small, this will lead to an exchange of adsorbed cations on the soil colloids (2). The desorbed ions will be leached out of the soil (3) and the degree of base saturation will be reduced (4). A more acid and a less nutritive state

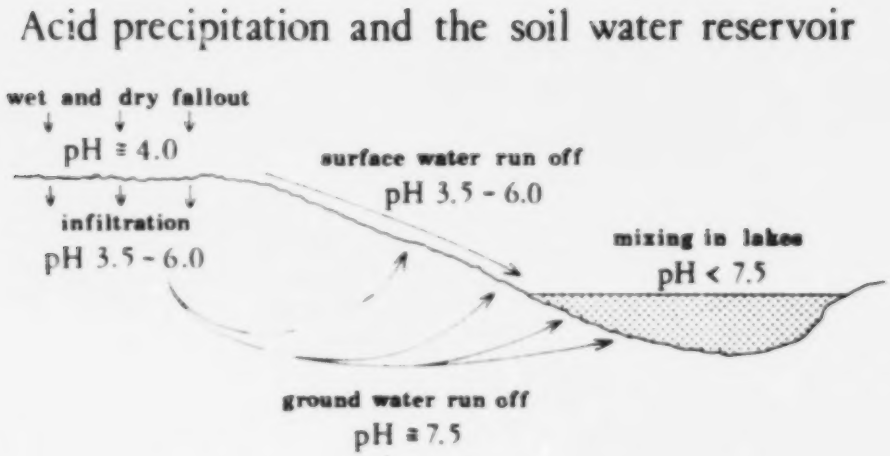


Figure 17. Part of the hydrological cycle related to soils and surface waters.

will have an effect on plant growth (5) and will change the composition of the plant community in the long run (6). Such biological changes are likely to give a feedback effect of increased acidification (7). Furthermore, the rate of mineralization of litter and humus will be retarded (8). Until a new equilibrium is obtained the cycling of nutrients in the ecosystem will be retarded, too (9). Some of these effects will to some extent be counterbalanced by increased weathering (10) of the soil minerals. On the other hand, when a soil type with accumulation horizons is affected, large amounts of ions, i.e. heavy metals, may start to dissolve (11). Processes of soil formation will be enhanced and less productive soil types will be formed (12).

Some of the 12 items above have been verified in our studies. Others have been formulated as postulates since they are derived from common knowledge in Soil Science or Soil Biology. It is only a matter of time and intensity before all effects are verified. Some examples are given below.

In 1970 we made a soil survey of forest soils in Sweden and Norway. Sites similar with respect to soil type and vegetation (185 places) were selected and samples were taken down to a soil depth of 50 cm. The maps for pH and the degree of base saturation are shown in Figure 18.

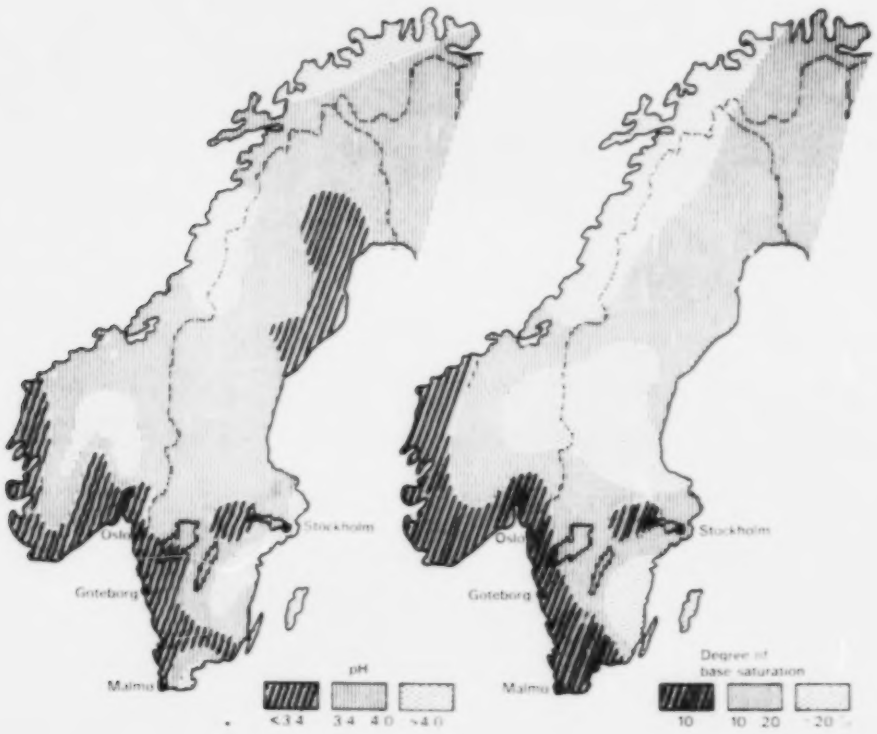


Figure 18. pH and the degree of base saturation at the upper 5 cm of podsolized forest soils in Scandinavia. From Sweden's Case Study.

There is a large continuous zone on the southwestern part of Scandinavia with lowest figures both in pH and in the degree of base saturation. This part is also closest (with respect to wind conditions) to the Center of acidity in Europe. A small area of similar soil changes occurs west of Stockholm. At a place within that area alum shale has

been burned for decades, giving rise to large emissions of SO_2. The effects on the soils, however, is only local.

The atmospheric acidity has for the most been related only to mineral acids like sulfuric acid, hydrochloric acid and nitric acid. The irreversible adsorption by the plants of any kind of cation will also give rise to increased acidity in soils and waters. Anions, on the other hand, will cause the reverse effect, i.e. making the systems more alkaline. Since the net effect of the ionic uptake by plants acidifies the systems, I have called this effect "biological acidification." When this concept is applied, for instance, to a peat bog, its pH-value around 4 can be adequately explained solely by processes of biological acidification. There is no room for humic acids or the like from an explanatory point of view.

NH_4-salts form a major part in the processes of biological acidification. As shown in Figure 3, this compound increases with time in the precipitation leading to increased acidification of soils and waters. At present, however, we do not know the exact figure for the total load (wet or dry) of acids or acid-forming substances. Our best judgment related to the southwestern part of Scandinavia amounts to 100 milliequivalents/m^2 per year or 1000 equivalents per ha per year. This is equal to 50 kg concentrated sulfuric acid. This figure is approximately 3 times higher than the figure used in the Swedish Case Study.

When the figure above is applied to a normal podzol in Scandinavia without calcareous materials in the subsoil we can compute the time necessary to desorb all the cations down to half a meter. The computation

gives a formal figure, which is always the case when residence time or turn over time are computed. We arrive at a figure of 150 years. Long before that time biological effects will have shown up.

As indicated by Figure 18 the soils in southwestern Scandinavia are already considerably depleted of cations. In comparison with a normal podzol these soils have lost between 55 to 70% of their original content of cations. The higher figure refers to the subsoil. Most of these losses, but not all, has to be attributed to changes of the chemical climate during the last 100 years.

Due to the very high heterogeneity in soil characteristics it is very difficult to determine chemical changes in soils over a short period of time. Data from the Swedish water quality network, however, gives some of the answers. Figure 19 gives an example from river Ätran (cf. Figure 2). SO_4-S has increased by more than 5 kg in 10 years. When the reduction of the agricultural use of fertilizer -S during the last decade is accounted for, this increase is actually 10% larger. HCO_3 decreases by almost 20 kg (cf. Figure 15) and the total amount of cations has increased by approximately 360 E/ha. In the form of $CaCO_3$ the last figure equals 18 kg/ha. pH is reduced by 0.2 units. The following identity can now be formulated, where X denotes processes of biological acidification.

$$391 + X = 360 + 283; \qquad X = 252 \text{ E/ha}$$

The reason for this identity is given by Figure 19. Biological acidification has increased by 252 E/ha during the last 10 years. The absolute value is not known at present. Total acidification in this part of Sweden has increased by 643 E/ha during the same time. Fifty-six

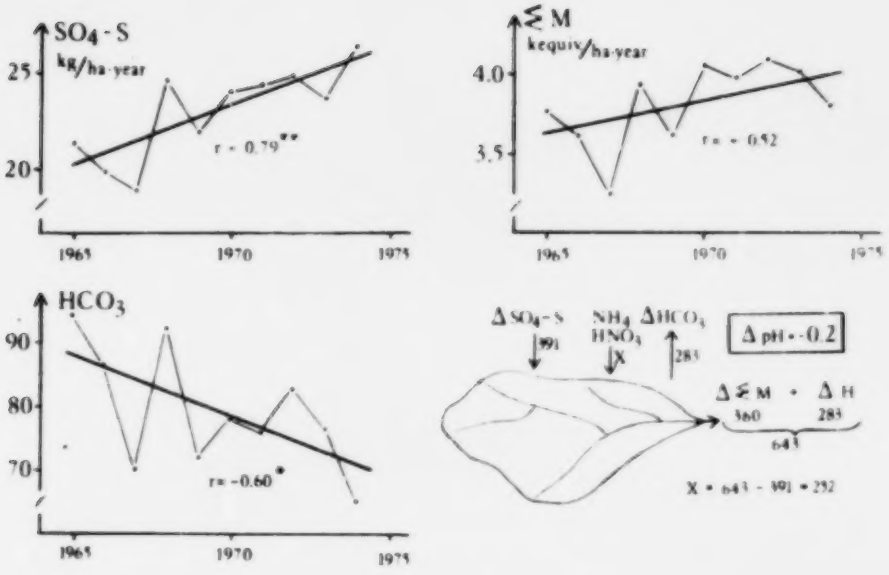


Figure 19. Discharge of SO_4-S, HCO_3 and the sum of cations (ΣM) from the drainage area of river Atran. Changes of these quantities during the last ten years are given in Equivalents/ha. X denotes the magnitude of processes of biological acidification.

percent of this impact of acids is neutralized in the soil by ion exchange and weathering. The remaining 44% suppresses the dissociation of bicarbonate leading to diffuse emission of CO_2 to the atmosphere. When HCO_3 is close to zero (pH of surface waters $\leq$ 5.6) the effect of a given amount of acids on the environment will consequently be almost doubled. This "point of no return" has apparently been passed in certain areas in Scandinavia. pH of about 4.5 are common in these areas where no local sources are known.

In order to document that the soil effects measured in southwestern Scandinavia are man-made (the opposite has been argued) a similar study around a copper smelter at Falun has been made. This smelter has been

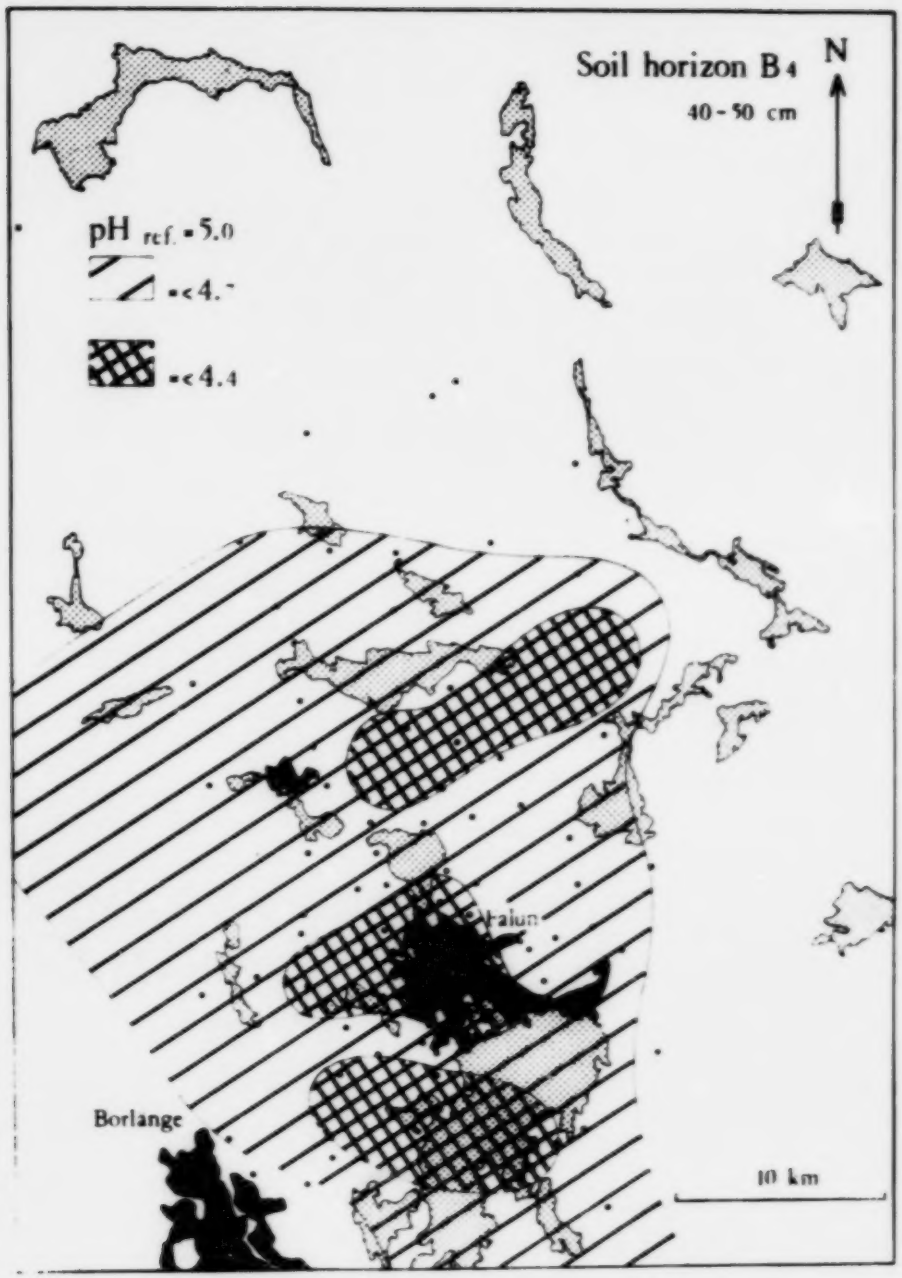


Figure 20. Changes in pH and the degree of base saturation in the soil around a copper smelter at Falun (150 km NW of Stockholm). The maps refer to a soil depth of 40 - 50 cm.

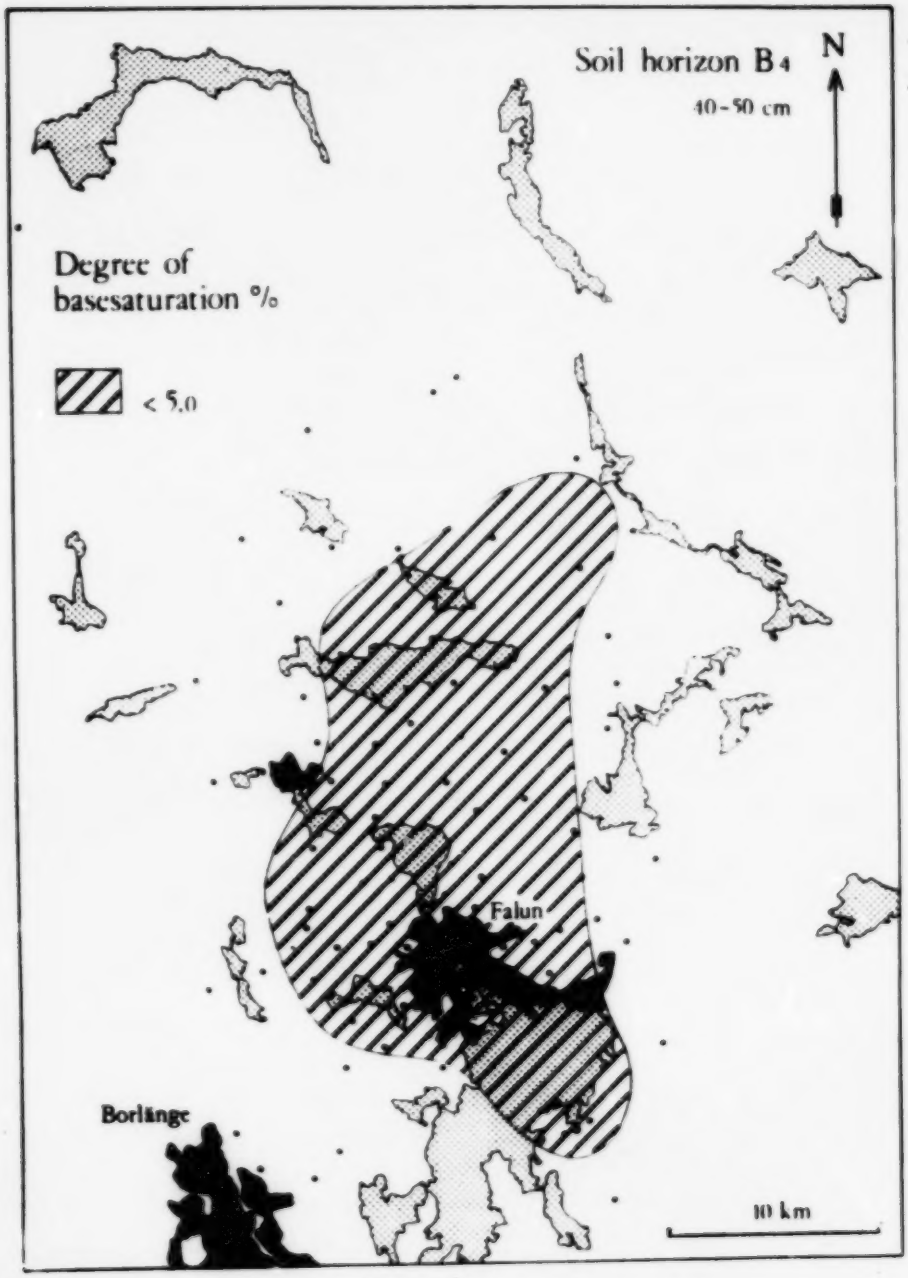


Figure 20 (Continued)

operating for about 500 years and the total emission of SO_2 amounts to some 5 million tons of SO_2 over this period. Some results are shown in Figure 20.

pH has been considerably reduced in all soil horizons even down to a depth of 40 - 50 cm. Close to Falun the acidity has increased more than 4 times with respect to a reference value of pH 5.0. In fact, the whole area within the map is influenced by increased acidity at this depth. The degree of base saturation is also considerably reduced. Far outside the map the degree of base saturation is about 25%.

The conditions within the shaded areas at Falun are chemically very similar to those in the southwest of Scandinavia with due regard to equal conditions of bedrock and soil parent material. The growth of forest trees has not yet been measured. According to growth results presented in the Swedish Case Study a reduction of growth, however, is likely to have taken place. The productivity of both pine and spruce has proved to be much lower when the soil content of calcium is reduced.

* * * * *

The framework and structure of the acidity problem, the effect on natural and human systems and the dimension of the problem with respect to time and space were outlined in 1968. The Swedish government acted promptly but in vain. And we are still far from a general agreement between countries in Europe to debate emissions of acidifying compounds. This is partly due to a variety of opposite positions (with respect to this presentation) taken by scientific and advisory personnel since 1968. Statements like "The idea of a reduced pH in precipitation in Europe is only hypothetical, since pH can not be measured in such an unbuffered solution" or "Increased fallout of acids is beneficial for pine trees

because they like acid conditions" seem not to be very constructive in order to tackle this large-scale problem.

Part of this paper was presented as a plenary lecture at the 19th Congress of the International Association of Limnology in Winnipeg in 1974 (Oden & Ahl: Man-made Changes of the Scandinavian Environment). The Congress adopted the following resolution:

"Whereas, the increased introduction of man-made pollutants to the atmosphere is seriously contaminating the earth's airsheds, often remote from local sources, and

Whereas, the fallout of these materials is contributing to acidification and other pollution of lakes, rivers, and groundwaters of large geographic regions, and,

Whereas, the recently observed, and projected changes in acidity of waters represent a serious stress for natural aquatic ecosystems,

Therefore, this Congress deplores such degradation of aquatic ecosystems, and urges government, scientists, engineers, and laymen everywhere to investigate thoroughly the ecological magnitude of these changes, and to undertake prompt and ecologically sound remedial action."

It is my sincere hope that the members of this New York State Conference will adopt these statements and transfer them to legislative actions.

Part of the work presented in this paper has been sponsored from time to time by the Research Council of the Swedish Environmental Protection Board. The Swedish Case Study was supported by the Government.

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ACID PRECIPITATION: OUR UNDERSTANDING OF THE PHENOMENON

Gene E. Likens*

Introduction

Our awareness and understanding of the phenomenon of acid precipitation in the United States is just beginning. It is believed that acid precipitation in the industralized northern Temperate Zone is caused by the oxidation and hydrolysis of gases (SO_2 and NO_x) in the atmosphere generated from the combustion of fossil fuels; only recently has the regional nature of the problem become apparent (Likens, 1972; Likens, et al., 1972; Likens and Bormann, 1974; Cogbill and Likens, 1974). Likewise, ecological and economic concerns have been recently formulated, but are largely unquantified in the United States. Thus we must start with a series of fundamental questions which prescribe the scope and foci of the problem.

Central Questions

The first question is: What would be the pH in an unpolluted area on a long term basis? That is a very difficult question to answer because there are no historical records of actual pH measurements of precipitation in the U.S. prior to about 1939 (Cogbill, 1975). So, as a point of reference the pH value, 5.6, has been taken as the lowest pH that could be produced by carbonic acid if pure water were in equilibrium with atmospheric carbon dioxide (Barrett and Brodin, 1955). Dr. Odén would use a pH value appreciably

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*Professor, Ecology and Systematics, Cornell University, Ithaca, New York, 14853.

higher than this (this symposium). In the northeastern United States we find that rain and snow are currently at pH's much lower than 5.6, i.e. precipitation is several hundred times more acidic than would be expected. Values of pH < 3.0 have been measured for individual rainstorms in the northeastern U.S. (Likens and Bormann, 1974). These lowered pH's are brought about by the presence of strong acids, sulfuric and nitric, in rain and snow (Galloway, et al., 1975).

A monthly record of precipitation pH for central New York and the White Mountain region of New Hampshire is shown in Figure 1. These data show that pH values throughout the year are appreciably lower than would be expected on the basis of a carbon dioxide equilibrium alone. They also show that over this large area of the northeastern United States the pH values are essentially the same. Summer pH values are generally lower than winter values; that is, summer rains are more acidic than winter snows. The average pH weighted for volume of precipitation over the course of a year then, at all of these locations (Figure 1), is about pH 4.

The next question is: What is the source of the acidity in precipitation? We've looked at this rather carefully in our studies of precipitation chemistry at Cornell. There are various potential sources of protons in precipitation (Table 1). In the left-hand column of Table 1 are the strong proton sources--the strong acids, sulfuric, nitric and hydrochloric - that dissociate fully in water to produce free protons. In the right-hand column are sources of bound protons in precipitation: carbonic acid, a generalized organic acid, clay particles, ammonium, aluminum and ferric hydroxide. These latter substances are all sources that could contribute to the total acidity of a solution, i.e., the acidity determined by

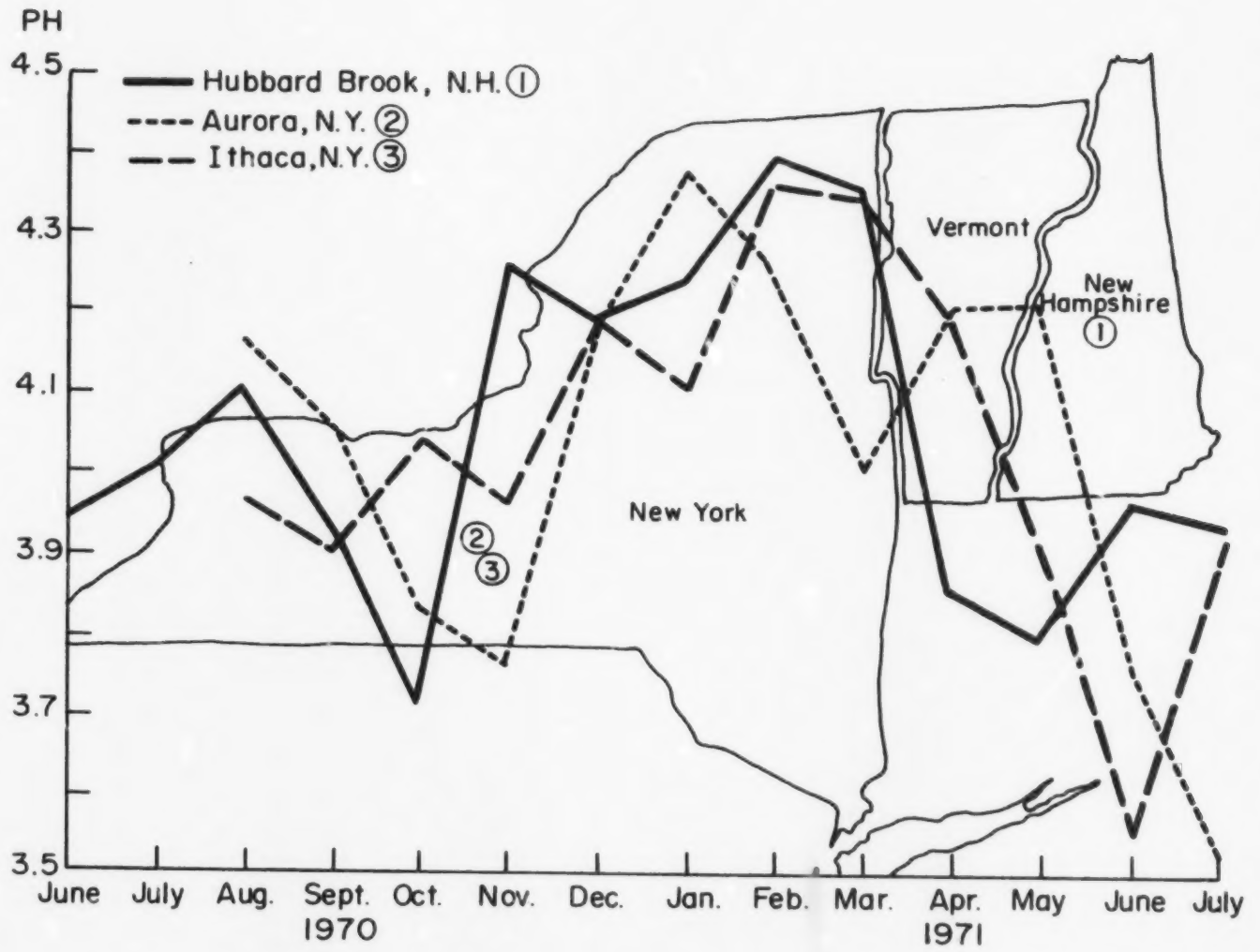

Figure 1. The pH of precipitation in the Finger Lakes region of New York State and at the Hubbard Brook Experimental Forest in New Hampshire (from Likens, et al., 1972).

Table 1. Proton Sources in Precipitation (from Galloway, et al., 1975).

Strong Proton Sources	Bound Proton Sources
H_2SO_4	H_2CO_3
HNO_3	RCOOH
HCl	Clay
	NH_4^+
	Al^{3+}
	$Fe(OH)_2^+$

titration with a base, but they provide bound protons rather than free protons in solution at pH's less than 5.0. The free protons can be measured with a pH electrode, bound protons cannot. We have evaluated the sources and relative proportions of free and bound protons in samples of precipitation from central New York, from the Hubbard Brook Experimental Forest in New Hampshire, and from the Adirondack region of New York (in association with Carl Schofield).

An example of the relative contribution of free and bound protons from each of the potential proton sources in a precipitation sample at pH 4.0 is given in Table 2. The concentration of each potential proton donor is typical of precipitation samples in central New York (Ithaca), in the White Mountains of New Hampshire or in the Adirondack Mountains of New York. At a pH of 4 there would be no contribution to the free (measurable) protons in solution from carbonic acid. One of the analytical difficulties when

Table 2. Sources of Acidity in Precipitation* in the Northeastern United States (from Galloway, et al., 1975).

	Concentration in Precipitation (mg/ℓ)	Contribution to Free Acidity at pH 4.0 (μeq/ℓ)	Contribution to Total Acidity in a Titration to pH 9.0 (μeq/ℓ)
H_2CO_3	0.62	0	--**
Clay	5	0	5***
NH_4	0.350	0	19†
Al	0.050	0	5
Fe	0.040	0	1
Mn	0.005	0	0.1
RCOOH	1.1	6	17
HNO_3 ††	2.1	34††	34
H_2SO_4 ††	2.9	60††	61◊

* Sample collected 27 February 1975 at Ithaca, New York.

** H_2CO_3 was removed from the system by N_2 purging. If the H_2CO_3 was not removed and the system was at equilibrium with the atmosphere, there would have been 5000 μeq/ℓ contribution to total acidity and no contribution to free acidity in a titration to pH 9.

***This assumes that all of the particulate material is montmorillonite clay; most likely the contribution to total acidity is an order of magnitude less than 5 μeq/ℓ because of minerals other than montmorillonite, which have a much lower exchange capacity.

† This assumes that all of the NH_4^+ is converted to NH_3 which is subsequently removed by the N_2 purge. The most likely value is between 7 and 19 μeq/ℓ.

†† The contribution to the free acidity is determined by a stoichiometric formation process in which a sea-salt anionic component is subtracted from the total anions (Cogbill and Likens, 1974).

◊ At pH 4.0, 1.5% of the total sulfate is present as HSO_4^-; thus total acidity for sulfate is greater than the free acidity.

determining the total titratable acidity of a precipitation sample is that great care must be taken to titrate the sample under nitrogen gas or some other inert atmosphere. If this were not done and the titration were conducted from say, pH 4 to pH 9, carbon dioxide from the atmosphere would be stirred into the sample and thus add a large artifact to the total acidity value. Unfortunately, this mistake is frequently made in analyzing precipitation samples.

Clay particles at a concentration of 5 mg/liter contribute no free protons to a precipitation sample at a pH of 4. Likewise, aluminum at a concentration of 0.05 mg/ℓ contributes no measurable protons; iron at a concentration of 0.04 mg/ℓ and maganese at a concentration of 0.005 contribute none; and ammonium at a concentration of 0.35 mg/ℓ contributes no free protons to a solution when the pH is 4. Thus none of these substances would contribute to the free acidity (ambient pH), but all of the substances could contribute to the total acidity of a sample of precipitation (Table 2).

We also have looked for some 33 different organic acids in precipitation, since it has been suggested that they could contribute significantly to the measurable acidity. We have found only one (isocitric acid), and it contributed 6 μeq/ℓ of the free protons at a pH of 4 (Table 2). Because a solution at pH 4 would contain 100 μeq/ℓ, the organic acid would contribute only 6% of the total free protons in solution. The remainder of the free protons (94%) are contributed by sulfuric and nitric acids. In all cases where we have looked carefully at the precipitation chemistry, the contribution of free protons in solution from the bound proton sources is very minor--less than 15%. The majority of the protons are contributed by strong

acids, sulfuric and nitric. Thus precipitation is currently a strong acid solution in the rural and semi-urban areas of northeastern United States.

The next question is: How long has the precipitation been dominated by strong acids? I've tried to look carefully at the historical record in this regard. It's very difficult, however, because I have been unable to find any actual pH data for precipitation samples prior to 1939, and no synoptic data prior to 1962 for the United States (cf. Cogbill, 1975). The earliest known measurement of precipitation pH in the U.S. was done on a single rainstorm in August of 1939 at Brooklin, Maine; a pH value of 5.9 was obtained (H. G. Houghton, personal communication). Then in August of 1949 at Washington, D. C. Landsberg (1954) measured the pH of eight individual raindrops with a microelectrode of a Beckman pH meter. The mean value of these eight drops was pH 4.2. In 1952-53 Landsberg (1954) measured the pH of individual raindrops during a large number of storms near Boston, Massachusetts, with pHydrion paper. The mean value was 4. These latter data from Landsberg (1952-53) have been taken to show that precipitation in the eastern U.S. was markedly acidic by 1952-53 (Cogbill, 1975). However, experiments with pHydrion paper in our laboratory have shown that the hydrogen ion content of individual raindrops may be overestimated by 5 to 6 orders of magnitude with this indicator paper. Conversations with the manufacturer (Micro Essential Laboratory, Brooklyn, N.Y.) have confirmed this, and in fact several milliliters of precipitation solution are required to make reliable determinations with the pHydrion paper. Thus measurement of individual raindrop pH by this method would be very misleading.

Obviously then, not enough actual data exist prior to 1962 to indicate areal, annual or seasonal patterns of precipitation pH for the United States. However, there exists detailed chemistry for some precipitation samples taken prior to 1950, particularly in Tennessee (1917-1922), in central New York State (1919-1928) and in Virginia (1923-1928). Also we found that it is possible to accurately "predict" or calculate the pH of precipitation if one knows the chemistry of a sample (Cogbill and Likens, 1974).

The stoichiometric relationship for calculating hydrogen ion concentrations is based on Granat (1972) and is shown in Figure 2. All cations and all anions in solution are summed and proportioned into their component parts. One component is attributable to a source in the sea (we call these sea-salt components) and contributes a certain amount of neutralized salts to the total solution. Some of the remaining acid-forming sulfate, nitrate and chloride anions, commonly referred to as excess ions, are neutralized by ammonium, calcium, magnesium, sodium and potassium ions in solution. There remain then an amount of sulfate, nitrate and chloride ions in solution that is balanced by hydrogen ion. We have found in present-day samples that we are able to predict this hydrogen ion concentration quite accurately from determinations of total chemistry (Cogbill and Likens, 1974). Predictions actually agree with measured values to within a few hundredths of a pH unit in almost every case we've analyzed from a variety of locations (including New York State, New Hampshire, Tennessee and Virginia). In practice it is very difficult to make a pH measurement in the field reproducable to better than 0.1 of a pH unit, so our calculated pH is an entirely satisfactory way of determining pH.

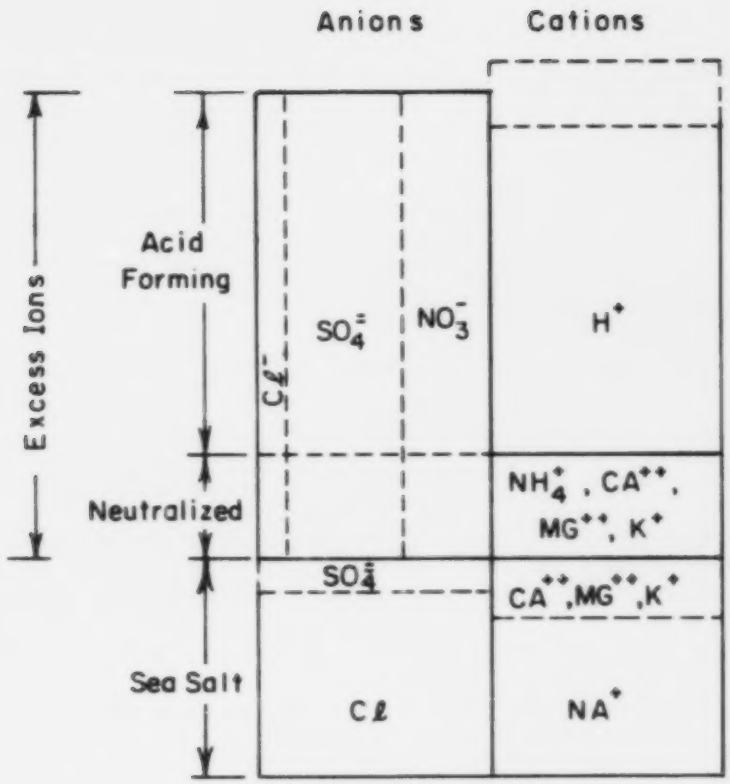

Figure 2. Theoretical ionic relationship between major chemical components in precipitation (from Cogbill and Likens, 1974).

Cogbill (1975) used this procedure to evaluate some of the early samples (prior to 1930) from Tennessee, central New York State, and Virginia. His results indicated that precipitation chemistry during this period was characterized by high ionic concentrations, but low acidity relative to present-day samples. Predicted pH's for these early samples ranged between 6.5 and 7.4. There also were some alkalinity determinations done on these samples using methyl orange and cochineal solutions; these results indicated that the samples obtained before 1930 were at pH's in excess of 6.9 (Cogbill, 1975).

However, since at least 1955-56, precipitation in the northeastern United States has been much more acidic (pH < 5.6). Using chemical data from Junge (1958) and Junge and Werby (1958) for 1955-56, we calculated the distribution of pH in the eastern U.S. (Figure 3). Based upon these data much of the eastern U.S., particularly the northeastern U.S., was being subjected to acidic precipitation by 1955-56. Magnesium values were not reported for these precipitation samples, but the maximum error generated by this would be less than 5%

The same procedure was applied to chemical data for the U.S. from the National Center for Atmospheric Research during the period 1960-66 (Lodge, et al., 1968), for North Carolina and Virginia during 1962-63 (Gambell and Fisher, 1966), and for New England and New York during 1965-66 (Pearson and Fisher, 1971). The pattern of precipitation pH that was predicted from this analysis for 1965-66 is shown in Figure 4.

It should be noted that the pH 5.6 isoline moved eastward and southwestward from 1955-56 to 1965-66, and that there was an intensification of acidity of precipitation in the northeastern region. The National Center

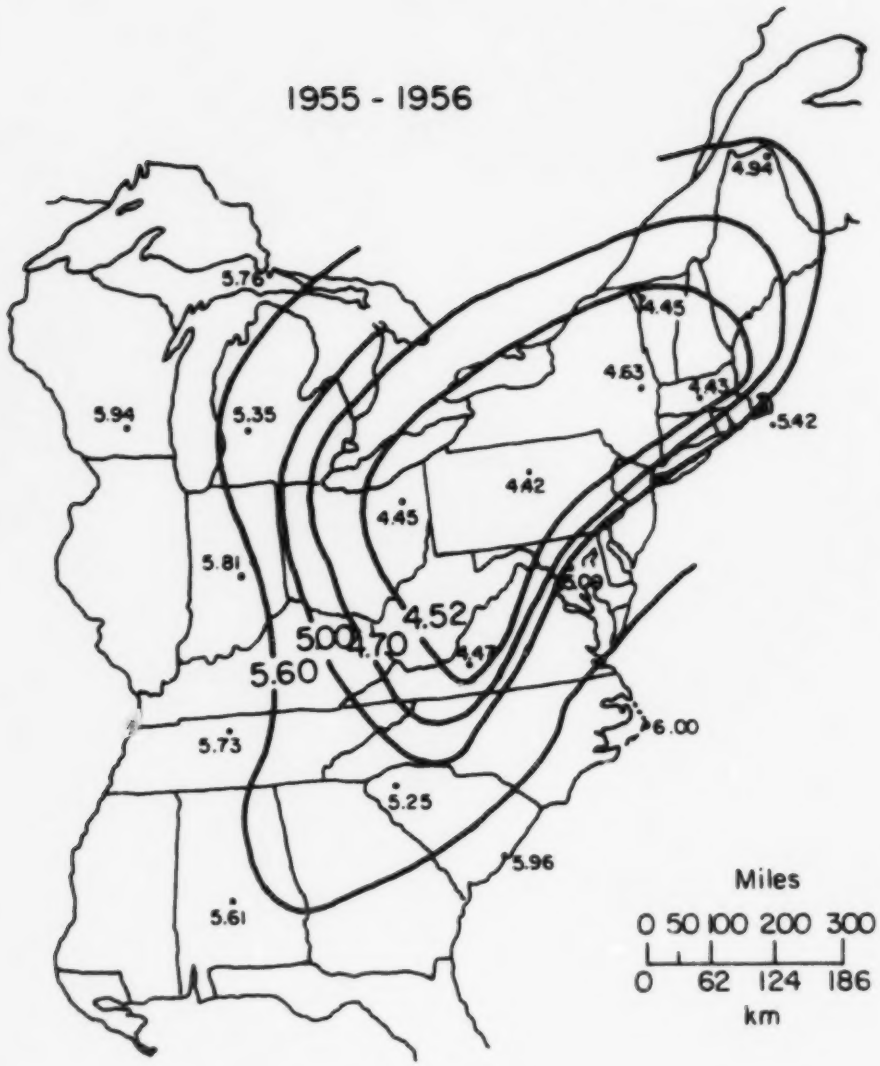

Figure 3. Predicted pH of precipitation over the eastern U.S. during the period 1955-56 (from Cogbill and Likens, 1974).

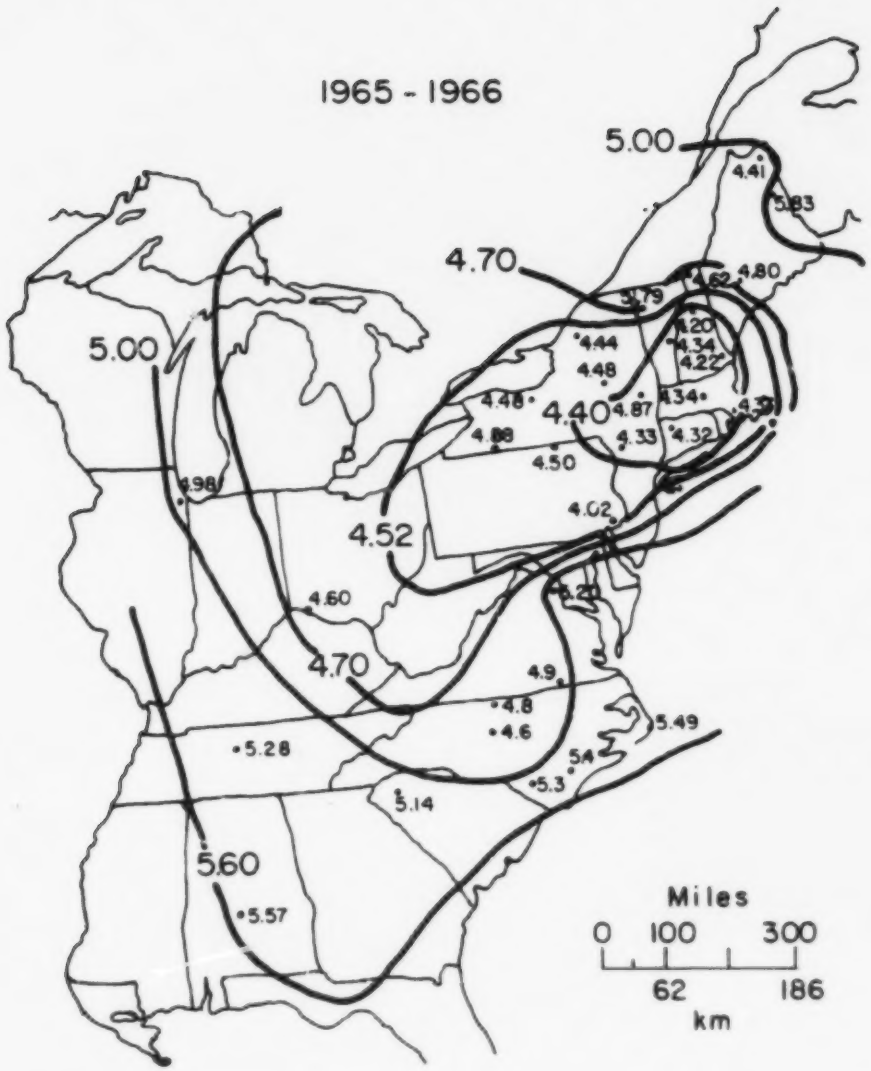

Figure 4. Predicted pH of precipitation over the eastern U.S. during the period 1965-66 (From Cogbill and Likens, 1974).

for Atmospheric Research also determined pH at 28 stations in the coterminous U.S. during 1964-66, but these data have never been fully published (Lazrus, et al., 1974). Values as low as pH 2.1 were measured during tnis period. Actual measured values for June, 1966, are representative of the pattern of pH values for the entire U.S. during 1964-66 and are shown in Figure 5. I think these data are of particular interest because I know of no other maps available for the entire U.S. which give any idea of the distribution of measured pH of precipitation over the course of a year. A study done by high school students during a two-week period in March, 1973, sponsored by "Current Science", also provided some data for the U.S (Strong, 1974).

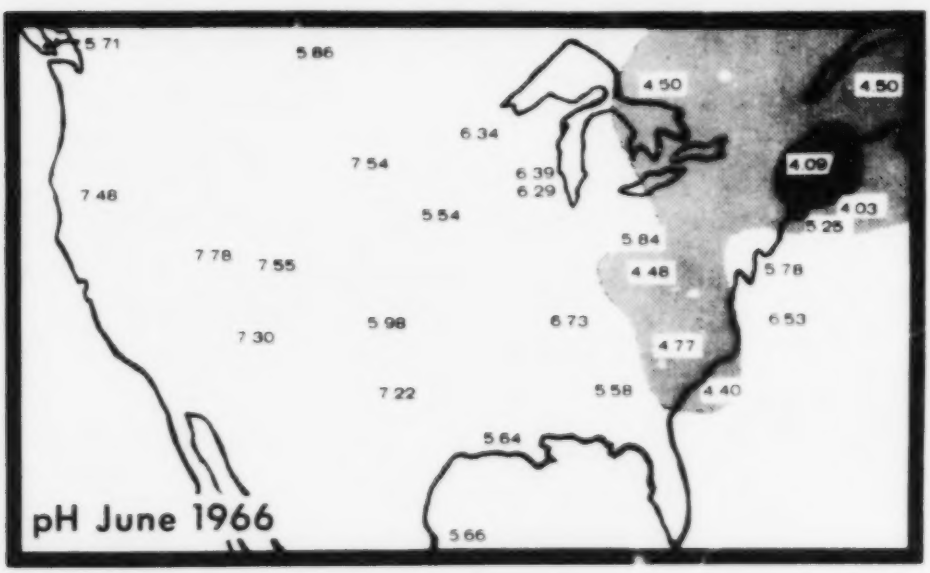

Figure 5. The pH of precipitation over the United States during June, 1966. Data courtesy of the National Center for Atmospheric Research (A. L. Lazarus, personal communication).

Clearly the northeastern United States is currently subject to acid precipitation, whereas the western U.S. is not (Figure 5). On occasion precipitation in the western U.S. may be highly alkaline because of dust scavenged by precipitation. These NCAR data corroborate nicely the predicted pH pattern for 1965-66 (Figure 4). This should not imply that within any of the "isoline areas" there won't be variation. There will be appreciable variation - "hot spots" around cities, and particularly around smelters. These geographical distributions are generalized patterns based upon available data.

Currently data are available to sketch a measured pH distribution map for the eastern U.S. (Figure 6). Again there appears to have been a further extension of low pH precipitation toward the west and southwest, and an intensification of acidity in the northeastern region. The small circle in southeastern Canada is the copper and nickel smelter in Sudbury, Ontario, which is a localized "hot spot." I also would call attention to the sharp northern boundary for the pH isolines. It appears that this may be a real boundary, and is suggestive of air movements in this region. The definition and significance of this boundary requires further study.

Current Trends - Hubbard Brook Ecosystem Studies

Studies of precipitation chemistry at the Hubbard Brook Experimental Forest since 1963 provide one of the longest comprehensive records for the U.S. Being downwind of eastern and midwestern industrial centers, the rural Hubbard Brook Experimental Forest offers a prime location to monitor long-term trends in atmospheric chemistry. Bulk precipitation samples are collected on a storm or weekly basis rather than the more commonly used

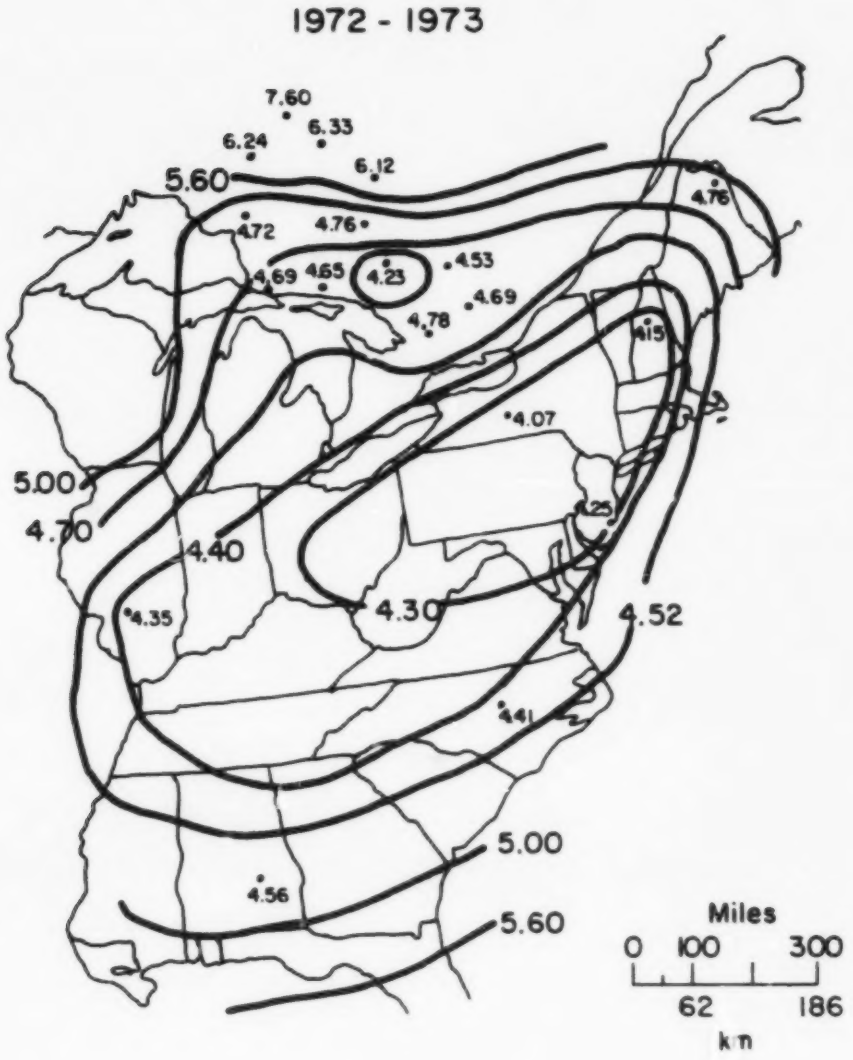

Figure 6. Observed pH of precipitation over the eastern U.S. during the period 1972-73 (from Cogbill, 1975).

monthly interval. Considering the problems of contamination and biogeochemical transformations that may occur in a reservoir of a precipitation collector in the field, our experiences have shown that sampling intervals of not longer than a week are highly desirable, if not necessary, to obtain accurate data on precipitation chemistry. In areas where dry fallout is more prevalent, sampling of individual precipitation events may be the only alternative to obtain reliable precipitation chemistry. At Hubbard Brook, dry deposition is a small proportion of the total wet and dry deposition.

Sulfate and hydrogen ions dominate the precipitation falling on the forested watersheds at Hubbard Brook (Likens, et al., 1976). On an equivalent basis $SO_4^=$ is 2.5 times more common than the next most abundant anion, NO_3^-, and hydrogen ion is 5.9 times more prevalent than the next most abundant cation, NH_4^+. On a long-term basis, the total negative equivalent value is 94.9% of the total positive value and cation and anion sums are not statistically different (Table 3). The determination of hydrogen ion is probably our principal analytical error in determining an equivalent balance. Hydrogen ion concentration was estimated from measurements of pH, and errors of the order of $\pm$ 0.05 pH unit would be sufficient to explain the discrepancy in the cation-anion balance. However, considering that these long-term averages include the various sampling and analytical errors over 8- to 11-year span, the agreement is quite good.

Thus we can say with confidence that precipitation at Hubbard Brook can be characterized as a contaminated solution of sulfuric and nitric acid at a pH of about 4.1. The average annual weighted pH during the period of 1964-65 to 1973-74 ranged between 4.03 and 4.21 (Figure 7).

Table 3. Weighted annual mean concentration in bulk precipitation for the Hubbard Brook Experimental Forest (from Likens, et al. 1975).

Substance	Precipitation 1963 - 1974	
	(mg/ℓ)	(μeq/ℓ)
Ca^{++}	0.16	7.98
Mg^{++}	0.04	3.29
K^{+}	0.07	1.79
Na^{+}	0.12	5.22
NH_4^{+}	0.22[a]	12.2
H^{+}	0.073[ab]	72.4
$SO_4^{=}$	2.9[a]	60.3
NO_3^{-}	1.47[a]	23.7
Cl^{-}	0.47[c]	13.3
$PO_4^{\equiv}$	0.008[d]	0.25
HCO_3^{-}	~0.006[e]	--
TOTAL	5.54	(+)102.9 (-) 97.7

[a] 1964-1974

[b] calculated from pH measurements on weekly samples

[c] 1965-1974

[d] 1972-1974

[e] calculated from H^{+} - HCO_3^{-} equilibrium

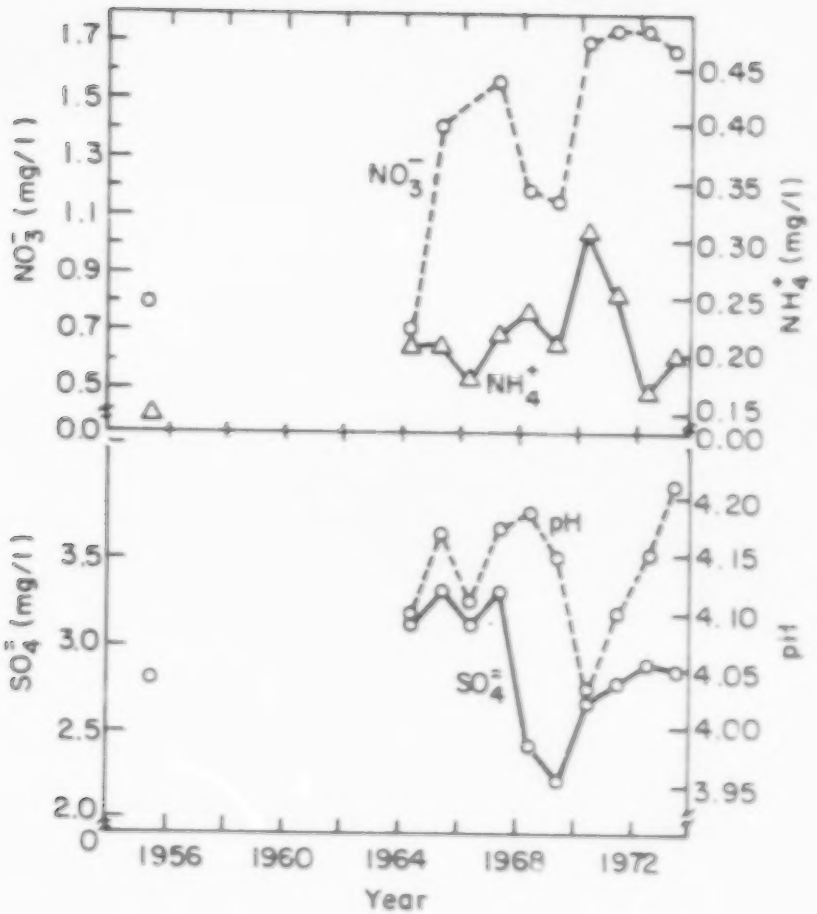

Figure 7. Annual weighted mean concentrations in precipitation for the Hubbard Brook Experimental Forest during 1955-1974. The values for 1955-56 were extrapolated from isopleth maps given by Junge (1958) and Junge and Werby (1958). Note that the ordinate has been compressed (from Likens, et al., 1975).

Rarely do pH values approach 5.0 and in the past year they have not exceeded 5.0 for any collection period. The lowest value reported for a single storm at Hubbard Brook was pH 3.0. Such precipitation is decidedly abnormal chemically, as discussed above. Furthermore, much of the dissolved and particulate matter normally present in precipitation would tend to increase the pH by several units. In other words, precipitation at Hubbard Brook has a hydrogen ion concentration 50 to 500 times greater than expected.

There was a downward trend in annual pH values between 1964-65 and 1970-71 followed by an upward trend until 1973-74. If we had sampled only during this period, we could have made a case of the fact that the pH was dropping dramatically, and precipitation was becoming more acidic. If we had started our studies in 1970, we could have made the opposite case, i.e. that the pH was increasing and precipitation was becoming much more alkaline. This points up the pitfalls of short-term data. No overall trend in annual pH values was statistically significant during the period 1964-1974 (Figure 7).

Likewise, concentrations of $SO_4^=$ and NH_4^+ vary from year to year, but there were no statistically significant trends for the decade. In contrast, annual NO_3^- concentrations currently are about 2.3-fold greater than they were in 1955-56 or in 1964-65 (Figure 7). The sum of all cations, except hydrogen ion ($\Sigma M^+ - H^+$), decreased from 51 ueq/ℓ in 1964-65 to 25 ueq/ℓ in 1973-74, which represented a 55% reduction in this component of precipitation during the period.

Even though the annual hydrogen ion concentrations were variable, the annual input (concentrations times volume) in precipitation increased by

1.4-fold during the period from 1964-65 to 1973-74 (Figure 8). Thus by 1973-74, more than 1.1 equivalents x $10^3 H^+$/ha-yr were being deposited on forested ecosystems at Hubbard Brook in precipitation. This increased input in hydrogen ion was in sharp contrast to the annual input of all other ions except nitrate (Table 4). Based upon a regression analysis, annual nitrate input increased by 2.3-fold during the decade. There was no significant increase in annual sulfate input during the period.

The increased annual input of hydrogen ion is partially explained by the significant increase in amount of annual precipitation during the 10-year period (Table 4), but data for individual years show that factors other than increased precipitation are important (Figure 8). In fact, hydrogen ion input is only weakly related to annual precipitation input (Figure 9). Thus other factors also are operative in regulating the annual input of hydrogen ion, and consequently annual weighted concentrations (pH) alone do not accurately reflect trends in total annual input.

The input of nitrate and sulfate also are directly related to the amount of annual precipitation (Figure 10). There is more variability in the sulfate relationship to precipitation than for nitrate, and in fact without the very wet and very dry years the relationship would not be meaningful (Figure 10). In contrast to hydrogen ion, sulfate and nitrate, the input of all cations (summed) except hydrogen ion is not related to amount of annual precipitation (Figure 9).

Surprisingly, the input of hydrogen ion was not significantly related to sulfate input over the 10-year period (Figure 11). Even though sulfuric acid is the dominant acid in precipitation at Hubbard Brook (Table 3), the annual input of sulfate did not increase significantly

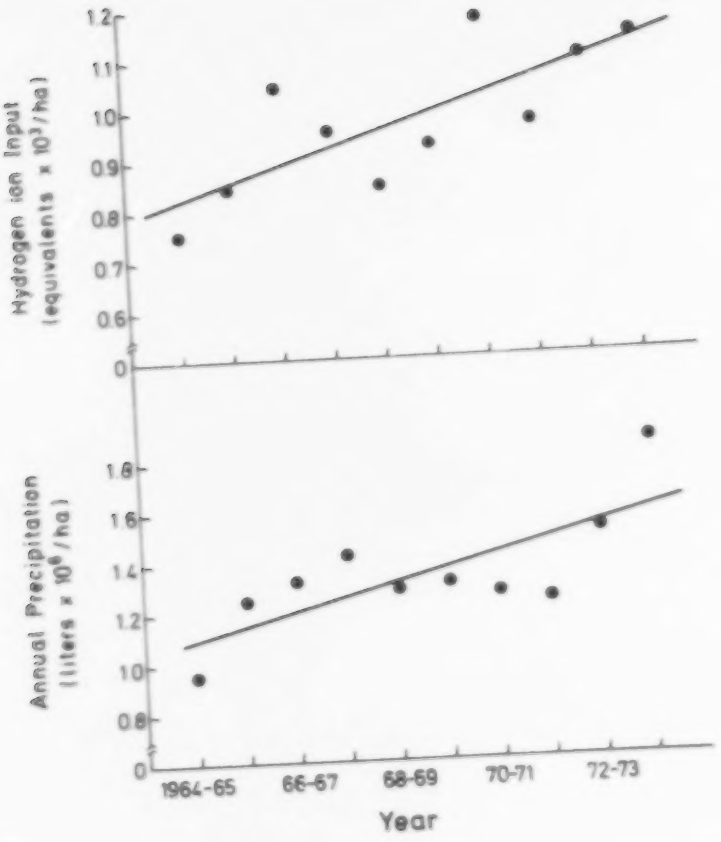

Figure 8. Annual hydrogen ion and water input in precipitation for the Hubbard Brook Experimental Forest. The regression line for hydrogen ion is $Y = 0.003X + 0.819$ where Y is the H^+ input in equivalents x 10^3 per hectare and X is the year. The significant correlation coefficient is 0.74. Note that the ordinate has been compressed (from Likens, et al., 1975).

Table 4. Regression analysis of annual precipitation input on year for the Hubbard Brook Experimental Forest (from Likens, et al. 1975)

Substance	Slope	Correlation Coefficient	Time Period
Ca^{++}	-0.174**	-0.83	1963-74
Mg^{++}	-0.046*	-0.66	1963-74
K^{+}	-0.126*	-0.66	1963-74
Na^{+}	-0.003	-0.02	1963-74
NH_4^{+}	0.110	0.57	1964-74
H^{+}	0.033*	0.74	1964-74
$SO_4^{=}$	0.279	0.32	1964-74
NO_3^{-}	0.388**	0.78	1964-74
Cl^{-}	0.300	0.22	1967-74
Water	4.96*	0.72	1963-74

* probability of a larger F-value < 0.05.

**probability of a larger F-value < 0.01.

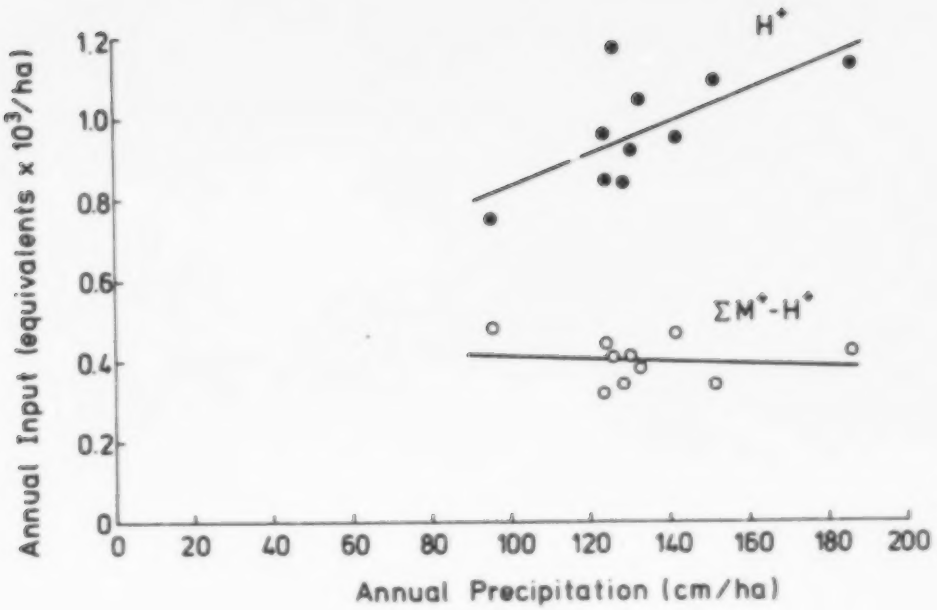

Figure 9. Relationship between annual input of hydrogen ion and all other cations except hydrogen ion (ΣM^+-H^+), and precipitation input for the Hubbard Brook Experimental Forest during 1964-1974. The regression line is $Y = 0.004X + 0.437$, where Y is the annual hydrogen ion input in equivalents $X\ 10^3$ per hectare and X is the annual precipitation in cm per hectare. The correlation coefficient is 0.67 and the probability of a larger F-value is < 0.05. The slope of the regression line for ΣM^+-H^+ is not significantly different from zero (from Likens, et al., 1975).

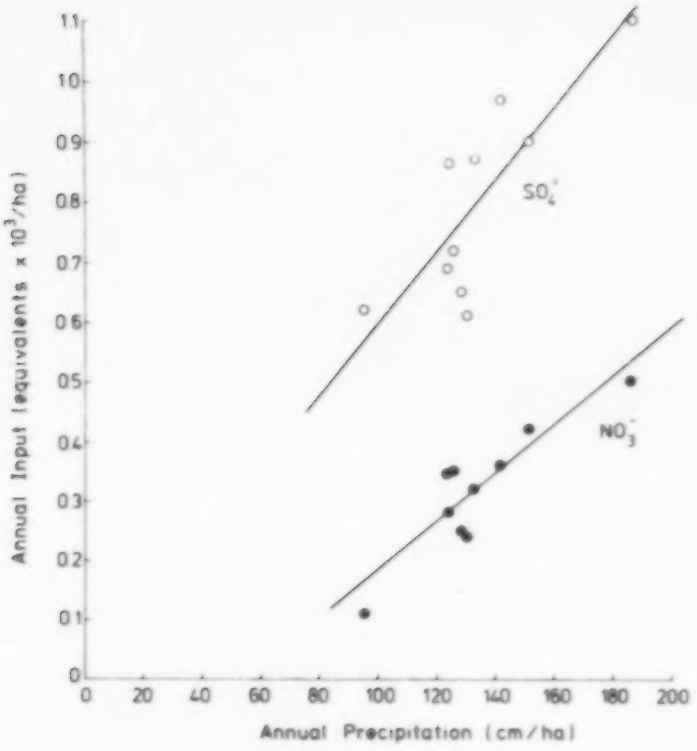

Figure 10. Relationship between annual input of sulfate or nitrate and annual amount of precipitation. The sulfate regression line is highly significant (correlation coefficient, 0.81) and the nitrate regression line is very highly significant (correlation coefficient, 0.90) (from Likens, et al., 1975).

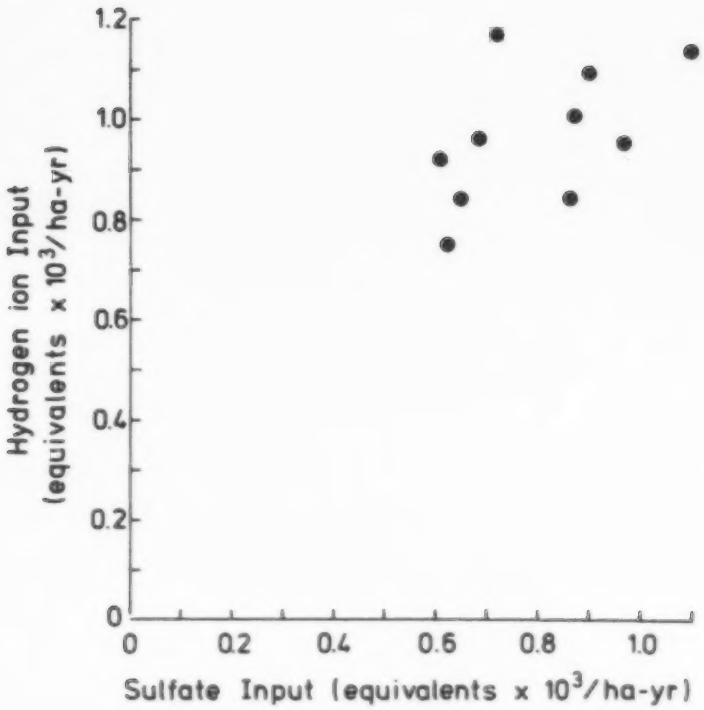

Figure 11. Relationship between the annual hydrogen ion input and the annual sulfate input during the period 1964-65 to 1973-74. The slope of a regression line fitted to these data was not significantly different from zero (from Likens, et al., 1975).

during the period, whereas the annual input of hydrogen ion did (Table 4). In contrast, the annual hydrogen ion input is highly correlated with the annual nitrate input during the past decade at Hubbard Brook (Figure 12). The 1:1 relationship between annual inputs of hydrogen ion and nitrate is a powerful argument that nitric acid is the crucial variable in explaining the increased input of hydrogen ion during the past 10 years.

Precipitation chemistry has changed both qualitatively and quantitatively at Hubbard Brook during the past decade. Absolute concentrations have varied (Figure 7) and relative proportions of the component chemicals have changed. Based on a stoichiometric formation process in which the sea-salt component is subtracted from the total anions in precipitation (Cogbill and Likens, 1974), the sulfate contribution to acidity dropped from 83% to 66% and nitrate increased from 15% to 30% from 1964-65 to 1973-74. Annual inputs reflect these changes in complex ways. In an attempt to resolve the relative importance of the various factors controlling the annual hydrogen ion inputs, a step-wise, multiple regression analysis was performed to relate the annual hydrogen ion input to a variety of independent variables. An analysis of five independent variables indicated that 86% of the variability in annual hydrogen ion input during the decade was related to annual nitrate input. Six percent of the variability was due to annual sulfate input, 5% to the input of the sum of all cations minus hydrogen ion, 2% to the year and less than 0.01% to the annual amount of precipitation.

I conclude from these studies that although sulfuric acid dominates the precipitation at Hubbard Brook and has for a decade, the increased annual input of hydrogen ion during the past ten years apparently has been due to an increase in the nitric acid input to this rural forested ecosystem.

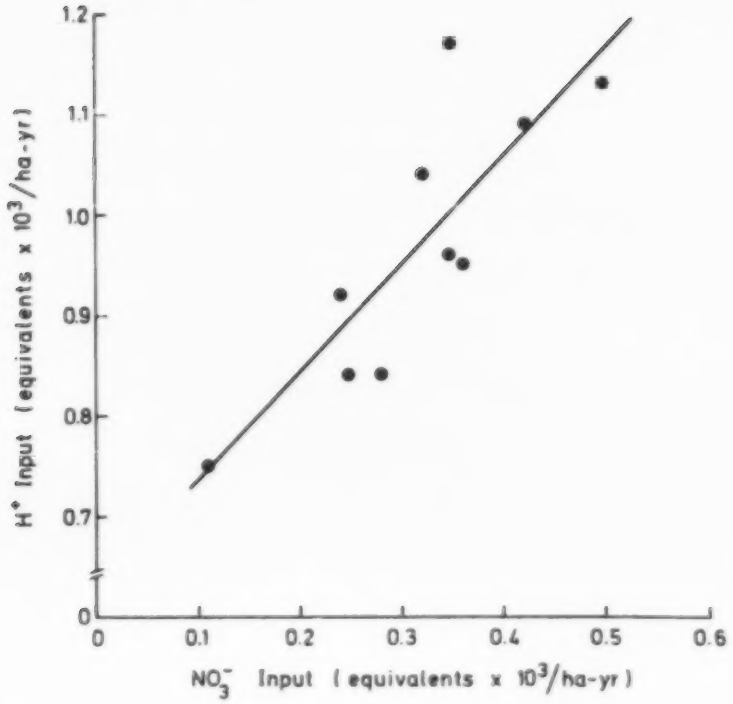

Figure 12. Relationship between the annual hydrogen ion input and the annual nitrate input during the period 1964-65 to 1973-74. The regression line: $Y = 1.07X + 0.631$, where Y is annual input of hydrogen ion in equivalents x 10^3/ha-yr and X is annual nitrate input in equivalents x 10^3/ha-yr, is highly significant (correlation coefficient of 0.84, and probability of larger F-value is < 0.01) (from Likens, et al., 1975).

General Remarks

These are the kinds of changes that we have seen in precipitation chemistry in a rural area of New England. There are now studies underway on the effects of these acidic inputs on the growth of forests, on streams and lakes, and on soils in the area. The geochemical effects at present seem to be minimal in the Hubbard Brook area (Johnson, et al. 1972), but we don't know whether there may have been a greater effect some 20-35 years ago as the precipitation became more acid. The biological effects on the forest may be significant (Whittaker, et al. 1974) but these data are difficult to interpret and will require further analysis and study (Cogbill, 1975). Dr. Carl Schofield will say more about the important ecological effects of acid precipitation on fresh water ecosystems.

I would like to add one final point. The acid precipitation problem has been shifted from a localized problem to a regionalized one, where acid precipitation is seen in widespread areas remote from the sources of SO_2 and NO_x. Acid precipitation is not a new phenomenon--acid rain and snow have been known and studied for at least 75 years, but the studies were on localized problems--localized around cities, near smelters, or close to fossil-fueled power plants. Recently this problem has been exacerbated by the increased combustion of fossil fuels and by the increased height of smokestacks, which tend to spread the pollutants over greater distances. The "philosophy" guiding the disposal of these combustion gases apparently has been similar to the old adage, "out of sight, out of mind." Much of our "waste treatment" follows this same kind of thinking. I would respond with another old adage: "everything that goes up must come

down." Apparently wastes being deposited on rural New York and New England as acid precipitation were "disposed of" great distances upwind.

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ACID PRECIPITATION: OUR UNDERSTANDING OF THE ECOLOGICAL EFFECTS

Carl L. Schofield*

I would like to preface my comments concerning our understanding of the ecological effects of acid precipitation by briefly quoting the introductory section of a document entitled "Recommendations to the Workshop Panels of the First International Symposium on Acid Precipitation in the Forest Ecosystem."

> "Scientists from many countries have convened at this symposium to define the present status of knowledge concerning changes in the chemical climate of the earth, especially those that cause acidification of rain, snow, soil and fresh water systems. These changes are inducing significant alterations in aquatic and terrestrial ecosystems. There is substantial evidence that these changes in the chemical climate are due in large part to increased emissions of man-made pollutants, but the extent and magnitude of their effects are not adequately understood. An integrated and international program of research is needed to deal with these problems. Therefore this symposium authorizes a set of workshop panels to formulate recommendations for research, to evaluate exchange processes between the atmosphere and natural reservoirs, and exchange reactions within these reservoirs especially those detrimental to life processes."

It goes on to list some fairly specific recommendations which I won't consider here. These panels were convened following the Ohio Symposium, and their recommendations will be published in the proceedings of the 1st International Symposium on Acid Precipitation and the Forest Ecosystem. The statements I've read indicate that significant alterations have been recognized in aquatic and terrestrial ecosystems. These alterations appear to have been induced by changes in atmospheric

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*Senior Research Associate, Department of Natural Resources, Cornell University, Ithaca, New York 14853.

chemistry. However, the extent and magnitude of these effects are not adequately understood, nor have they been thoroughly assessed.

The Ohio Symposium attempted to assess the effects of acid precipitation on aquatic systems, forest soils and specifically, forest vegetation. Not considered were agricultural systems and the structural damage to man-made components that Professor Odén mentioned yesterday. Problems related to forest soils and vegetation are not within my area of expertise, and I would not presume to evaluate them to any great extent at this time. I will highlight only a few of the significant problems relative to terrestrial systems and leave further discussion, additions, or clarification to others in this audience more knowledgeable than I in this field.

Acute effects of acid precipitation on soils and vegetation have been clearly identified only under extreme conditions, either experimentally induced or in situations very close to sources of heavy air pollution (e.g., Sudbury, Ontario). The relative significance of strong acids and associated heavy metals found in heavily polluted areas, has not been clearly established in terms of toxic effects on plants and soil organisms. The most serious consequence of regional acidification at currently observed levels may be the increased rate of leaching of major elements and trace metals from forest soils and vegetation. This is true both for the forest ecosystem and for the aquatic systems receiving these effluents. The increased mobility of certain elements such as aluminum, manganese and zinc, particularly at low pH, could be viewed as a very serious consequence in terms of their toxic properties at low pH; and for aluminum especially because of its role as a proton

donor and acid buffer. Sandy soils, low in exchange capacity, appear to be potentially the most sensitive to strong acid atmospheric deposition. Very acid podzols or highly calcareous soils represent extremes in soil pH; however, both types possess higher exchange capacity and relatively greater resistance to change in pH or free hydrogen acidity. The change in pH or increase in free hydrogen ion concentration may not be the most significant factor involved in the soil acidification process. Increased mobility of aluminum and iron, which may have direct toxic effects on plants, can additionally interfere in processes such as phosphorus transport in germinating seedlings.

Being more familiar with aquatic systems and since they also appear to be most sensitive to a phenomenon such as acid precipitation, I will confine the remaining discussion to problems associated with atmospheric inputs to dilute lakes and streams. One point I would like to make absolutely clear. Precipitation currently falling on remote areas in the northeastern United States, Scandinavia, and parts of Europe, is an acutely toxic medium to fish and other aquatic organisms. The average concentrations of strong acids and heavy metals found in precipitation from these areas greatly exceeds the known tolerance levels of many organisms inhabiting the lakes and streams in these regions. Obviously aquatic systems cannot be likened to "rain barrels" and certainly the soils and vegetation of the drainage basin will modify the chemical composition of lake and stream waters to varying degrees. The major questions are then: to what extent, how, and under what conditions are the toxic components of acid precipitation reduced or increased in natural systems and what are the responses of the biota to these modifications?

The significance of atmospheric contributions to the chemistry of dilute surface waters was first demonstrated quite clearly by the work of Gorham (1958). He compared the major ion content of waters in the English lake district to precipitation inputs and found that lakes lying in areas of hard, resistant bedrock received most of their major ion supply from precipitation and were correspondingly very dilute. It is also quite evident that this atmospheric-lake water chemistry relationship is dynamic and anthropogenic induced changes in precipitation chemistry will be reflected in the chemical and biological composition of dilute surface waters in sensitive regions. "Sensitive regions" are defined as North Temperate Zone geologic provinces, characterized by igneous or metamorphic bedrock, shallow soils, and the presence of acid precipitation. Extensive areas in Sweden and Norway, localized sections of the Canadian Shield in Ontario, and the western slopes of the Adirondack Mountains of New York State represent regions where lake and stream acidification has resulted in severe ecological damage (Wright, 1975; Beamish, 1975; Schofield, 1975).

At the risk of being somewhat provincial, I'd like to consider one of these areas, specifically the Adirondacks, with which I am most familiar, and utilize this as an example of how atmospheric inputs relate to surface chemistry in dilute waters.

The Adirondack Mountains are located in the northern part of New York State. A substantial lake district, consisting of about 2,300 lakes, is distributed throughout the region in a northeast - southwest orientation. The areas of highest elevation are in the east central and south to west quadrant of the Adirondack province. Geologically,

the area belongs to one of the oldest mountain formations known in eastern North America, and the bedrock consists principally of anorthosite and granitic gneisses. The soils are predominately acid podzols, but regional differences in soil pH and calcium content reflect differences in development that have occurred since the last glaciation, primarily in response to climatic variations in the region. The atmospheric flow affecting this particular area comes principally from the land mass of the North American continent. The high mountains in the souther and western areas intercept moisture laden air masses, resulting in orographic precipitation effects. Precipitation is heavy in the high mountain areas and much of this occurs as snow in the winter months. A large proportion of the runoff occurs as snowmelt in the spring. The precipitation falling on this area is quite acid and exhibits pH values as low as 3.5 in the summer; however, the weighted annual averages more closely approximate pH 4.2. There are strong acids present in this precipitation and they constitute 80 - 90% of the total titratable acidity.

As expected, based on these rather severe climatic conditions and edaphic conditions, the lakes and the streams of the region are very poorly buffered and usually of low pH. The lakes and streams exhibiting the highest levels of acidity are found in areas of high elevation, principally those lying at elevations greater than 2,000 feet. Most of the alkalinity, or capacity to neutralize acids in lakes at lower elevations is due to bicarbonate derived from weathering of silicate minerals, rather than crystalline limestones which are rare in this region. The soils developed from glacial deposits at the lower elevations

significantly increase the major cation (Ca, Mg, Na, K) supply in the drainage systems of these lakes and it is principally the higher calcium concentrations which offset excess atmospheric sulfate inputs. In contrast, sulfate replaces bicarbonate as the major anion in the high elevation lakes, because of the presence of strongly leached, base deficient soils in the comparatively small drainage basins. Strong hydrogen acidity develops in the presence of excess sulfate and buffering by aquo-metal ions such as aluminum and iron become significant. The development of low pH (4-5) conditions in these high elevation lakes due to the presence of strong acids (principally H_2SO_4), is clearly dependent on the balance between cation supply from the drainage basin and the loading of excess acid forming anions in precipitation. The extreme sensitivity of these poorly buffered, high elevation lakes to acid loading from atmospheric sources can be demonstrated by modeling the mass balance of major ion inputs. For example, an increase of 0.5 ppm SO_4 in Adirondack precipitation (annual weighted average concentration) over current levels, would be sufficient to increase the hydrogen ion concentration in a 2,000 ft. elevation lake having zero acid neutralizing capacity (pH $\sim$ 5.6) one order of magnitude ($\sim$ pH 4.6).

The marked temporal fluctuations in pH that occur in streams and lakes with relatively short retention times exemplify the significance of acid precipitation effects on a short term basis. Increases in hydrogen ion concentration of 10 to 100 fold have been observed in Adirondack streams and lakes during periods of snowmelt. Fish mortality is known to occur during these events; however, the extent and significance of this phenomenon to the eventual extinction of populations is as yet unknown.

Hultberg (1975) observed sharp pH drops under ice cover in Swedish lakes during spring thaws and attributed this to ion separation of pollutants stored in the snowpack. Wright (op cit) described the same phenomenon in Norwegian streams, where massive fish kills have been observed during spring snowmelt periods.

Long term changes are somewhat more difficult to assess due to the general lack of historical data. Looking at some of the changes that occur within fish populations as they tend to go to extinction, I think we can see a common factor that is involved both in the Adirondack lakes and those that have been studied in Sweden and Norway. Low levels of acidity (e.g. pH 4.5-5.0), which are tolerated by some species of adult fish, do interfere with reproductive processes to the extent that recruitment failure often results. The size and age structure of a fish population may shift to one where only a few large and old individuals remain prior to extinction. This same effect has been noted in acidified Canadian lakes by Beamish (1975) in the vicinity of Sudbury, Ontario.

Different causes have been ascribed to this reproductive failure and perhaps some or all may be involved. It was suggested that there is a failure in ovarian maturation in females due to acid stress. It has also been indicated that there are loss of fry, particularly for spring spawning species that are subjected to low pH values for the snowmelt. What is actually involved in each case we do not as yet know. We also see somewhat more subtle changes in some lakes that have become marginally acid. For example, increased growth rates have been observed in populations where decreased recruitment has lowered population densities to the extent that food availability for the remaining individuals is increased.

There are factors other than hydrogen ion concentration that are important in determining survival or relative survival of fish in aquatic systems. One is the total ionic strength of the system or concentration of other ions. High calcium and sodium concentrations ameliorate the effects of hydrogen acidity. In contrast, synergistic components such as zinc and copper may greatly accelerate death times in acid waters.

It was pointed out yesterday that there were increases in the lead concentration of the Greenland snowpack since the Industrial Revolution. This increased atmospheric loading of metals has been noted in biological systems as well. Heavy metals concentrations found in samples of mosses collected across Sweden during the period 1850 to the present indicate a trend of increasing concentration. Atmospheric deposition of zinc and lead is high in the northeastern area of the United States. The point is that just considering possible contribution of metals from this source alone to aquatic systems, the resulting concentrations are very close to those known to produce chronic or even acute toxic effects in some species of fish. In combination with the problem of acid waters the situation could become particularly severe.

I think there are other unknowns involved concerning the process of acidification in relation to the role of heavy metals, their sources, and synergistic effects. We have to be concerned with the relative significance of acute versus chronic responses in biological systems. The chronic responses are often very difficult to identify, particularly those that relate to changes in growth or reproductive failure as examples that I've mentioned. We know very little about the relative sensitivity of various species at different trophic levels in the ecosystem to acidification processes

and even less of community and ecosystem responses. Grahn (1975) described some rather marked feedback mechanisms that may occur in some lake systems when acidification occurs. This involves the incursion of normally terrestrial plant species such as Sphagnum into the littoral zone of the lake and an acceleration of the acidification process. Other changes occur at the decomposer level and involve shifts from bacterial to predominately fungal decomposition. There are many other facets of the acidification problem that need further investigation, particularly in relation to the processes and rates of change involved. At the present time our understanding of the ecological effects of lake and stream acidification is primarily descriptive in nature. Intensive lake studies and carefully designed monitoring programs will be required to enhance our understanding of the acidification process.

QUESTIONS AND ANSWERS

Q: Based on your analysis of changes in fish populations in the Adirondack lakes, what is your assessment of the overall changes in the Adirondacks in terms of fish populations?

A: The only place we've seen very marked changes have been these rather remote, high elevation lakes. We don't have a complete assessment for the whole Adirondacks, and what we're trying to do now is evaluate the changes observed within this group of high elevation lakes, which is a statistically definable system.

Q: What is the number of lakes affected?

A: Based on the survey data that I am now completing, something on the order of 50 - 60% of the total number of lakes over 2,000 feet in elevation are devoid of fish life.

Q: That's with no fish populations now, but where fish were known to be present previously?

A: No, we don't have that kind of information. I'd say that in about 15 to 20 lakes we know positively that there were fish populations present at times in the past and that currently there are none. There are many more acid lakes where there are no data relative to fish populations.

Q: Just thinking about the acidity and the snowmelt contribution, why don't the lakes remain acid during the summer?

A: Some of them do. Lakes with small watershed to surface area tend to maintain low pH throughout the year. In smaller systems, where the retention time is less, there's a subsequent input of groundwater and surface runoff that has significant acid neutralizing capacity and the pH tends to increase during the summer.

Q: If precipitation acidity should decrease, would water quality in affected lakes improve?

A: Well, I think we can get an approximation from seasonal observations in systems with short hydraulic retention times. The question whether responses would be forthcoming in the long term will depend on what is happening in the soils, about which we know very little. If there are no significant changes in soil chemistry, then one should expect improvement in lake water quality over a relatively short period of time, corresponding to the flushing time of the system.

Q: You cited data by Gorham, and you mentioned that that data has an atmospheric relationship to aquatic life. I really don't understand that statement.

A: What I've been trying to say primarily is that the acids found in some of these lakes are strong acids, predominately sulfuric, and they seem to originate from atmospheric sources. Excess anions in the system originate primarily from atmospheric sources.

Q: You really don't relate those acids (sulfuric and nitric) in water to ambient measurements in the air?

A: No, not to gaseous precursors, only to acid end products dissolved in precipitation.

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HEALTH EFFECTS OF ACID AEROSOLS

Jean G. French*

The major research effort in the study of adverse health effects of air pollutants in the past has centered around the primary pollutant such as sulfur dioxide (SO_2) and nitrogen dioxide (NO_2). We have now come to realize that the transformation products may be more toxic than the primary pollutants themselves.

Recent reports emanating from epidemiologic studies carried out as part of the Community Health and Environmental Surveillance System of EPA indicates the levels of suspended sulfates associated with certain adverse health effects were lower than the levels of SO_2 and total suspended particulates (TSP) associated with the same health effect.

A study of asthmatics carried out in the Metropolitan New York area showed that when temperatures rose to 30-50°F dose related increments in asthma attacks were associated with increments in total suspended particulates and suspended sulfates but not sulfur dioxide. The estimated threshold level for total suspended particulates was 56 ug/m^3 while that for suspended sulfates was 12 ug/m^3 (Finklea, Farmer et al., 1974). In a similar study of asthmatics in the Salt Lake Basin, the highest morbidity rates were associated with elevated suspended sulfate levels (Finklea, Calafiore et al., 1974).

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*Epidemiologist, Human Studies Laboratory, National Environmental Research Center, United States Environmental Research Center, Research Triangle Park, North Carolina 27711.

In a study of cardiopulmonary patients in the New York Metropolitan area, the strongest and most consistent pollutant effects were associated with suspended sulfates for aggravation of such symptoms as shortness of breath, cough and increased production of phlegm. There was evidence that annual average suspended sulfate levels of 10-12 ug/m^3 was accompanied by morbidity excess which averaged about 6% when temperatures were 30 to 50°F and 30% when temperatures were greater than 50°F (Goldberg, et al., 1974).

Since these initial studies, subsequent studies of asthmatics in the New York-New Jersey Metropolitan area and in two communities in the southeast support previous findings that exposure to elevated levels of suspended sulfates when accompanied by elevated temperatures may contribute to excess risk of asthmatic attacks. These later studies also showed that suspended nitrates may have a similar effect and in some instances the combination of elevated suspended nitrates and suspended sulfates seemed to exert a greater effect than either pollutant alone (French, et al.).

The associations found in these epidemiologic studies by themselves are insufficient to incriminate suspended sulfates and suspended nitrates as causative agents of certain adverse health effects. However, when these findings are coupled with those from experimental animal studies, the observations appear more than spurious and a rationale for the pathogenesis of the observed effect begins to emerge.

Studies conducted by Amdur (1969) using the guinea pig as the primary model, have shown that in terms of comparative toxicity sulfuric acid and some metallic sulfate compounds such as zinc ammonium sulfate are

more potent irritants than sulfur dioxide gas. Amdur found that if the particle size of zinc ammonium sulfate and sulfuric acid is essentially equivalent, sulfuric acid has the greater irritant potency. However if the zinc ammonium sulfate is present in a finer state of dispersion than the sulfuric acid, the zinc ammonium sulfate is the more irritating. As a gas, 1 ppm of sulfur dioxide produces an increase of about 15% in flow resistance. If through reaction in the atmosphere this amount of sulfur was converted to 0.7 u sulfuric acid, it would produce a resistance increase of about 60 percent, a four-fold increase in irritant response. If the equivalent of SO_2 were converted in the atmosphere to zinc ammonium sulfate of 0.3 u, the response would be about a 300 percent increase in resistance, a twenty-fold increment.

In other studies Amdur took both water soluble and insoluble non-irritating aerosols and combined them with sulfur dioxide gas. These experiments resulted in an increase in the irritating potential of the water soluble aerosols combined with SO_2 but no discernible change in the insoluble aerosols combined with SO_2. Amdur concluded from these studies that the major mechanism underlying the potentiation of the irritating effect of particulate material on the response to sulfur dioxide is solubility of sulfur dioxide in a droplet and subsequent catalytic oxidation to sulfuric acid (Amdur, et al., 1968).

Recent experiments by Frank and McJilton (1973) confirm Amdur's findings and indicate the importance of relative humidity in the response of animals to the SO_2/sodium chloride atmosphere. Guinea pigs were exposed for one hour intervals to atmospheres of 40% and 80% relative humidity. Significant changes in pulmonary flow resistance occurred only

in the combined SO_2/sodium chloride aerosol atmosphere at high relative humidity.

In a study conducted by Hazelton Laboratory (Alarie, et al., 1973) groups of cynomolgus monkeys were exposed for 78 continuous weeks to sulfuric acid mist at concentrations varying from 0.38 to 4.79 mg/cu m and particle size varying from submicronic to 4u mass median diameter (MMD). The results signified concentrations of 2.43 and 4.79 mg/cu m with particles of 3.60 u and .73 u MMD respectively, were sufficient to produce definite deleterious effects on pulmonary structures and deterioration in pulmonary function. Microscopic changes observed were principally characterized by focal epithelial hyperplasia and focal thickening of the bronchiolar walls.

Fairchild, et al. (1975) recently reported that a short-term high concentration exposure to H_2SO_4 aerosol (15 mg/m^3, 3.2 micrometers count median diameter [CMD]) slowed the rate of clearance of non-viable, radiolabelled streptococci from the nose and lung of mice. Inhalation of a small aerosol particle (1.5 mg/m^3 0.6 micrometers CMD of H_2SO_4) did not alter the clearance rate.

In another experiment Fairchild, Stultz, and Coffin found that a 60 minute exposure to 3020 ug/m^3 H_2SO_4 (1.8 um CMD) resulted in a 60% greater deposition of radiolabelled streptococcus aerosol in the naso-pharynx of guinea pigs. When guinea pigs were exposed to 30 ug/m^3 H_2SO_4 (0.25 um CMD) there was a significant increase in deposition of the radiolabelled streptococci in exposed vs controls but the site of increased deposition shifted to the trachea. The author hypothesized that H_2SO_4 inhalation may induce increased air flow resistance which may result in altered patterns of regional deposition of particles in the respiratory system.

The aforementioned studies are not without certain limitations. Most of the animal studies represent the work of one investigator using the guinea pig as the principal model. A major limitation in the Epidemiologic studies is the inability to characterize the measured sulfate compounds in terms of their physical and chemical properties. This poses a problem in trying to replicate the findings with respect to suspended sulfates and nitrates since the chemical composition of these pollutants may vary from one area to another and even within the same community over time. It is also possible that sulfuric acid and nitric acid in the ambient air are converted on the sampling filter and then measured as sulfates and nitrates.

Presently special effort is being devoted by EPA Research and Development to address the problems of measuring and characterizing acid aerosols in ambient air.

I have attempted to describe the health effects which have been identified with inhalation of certain acid aerosols in ambient air. What has not been properly addressed is the interface of these acid aerosols with water and soil and potential health problems from ingestion. Very little research has been conducted in this area.

It is possible that acid rainfall from nitric acid might ultimately lead to increased ingestion of nitrates. In the body nitrates may be reduced to nitrites by microbiological agents and cause problems such as methemoglobinemia. The presence of precursor amines and nitrite in the body also produces the potential for the formation of nitrosamines. It has been suggested that the protonation of nitrous acid appears necessary for initiating all nitrosation reactions and that carcinogenic

N-nitrosocompounds in quantities considered to be potentially hazardous cannot be produced unless the interaction of nitrite and amine occurs in acidic medium (Ender, et al., 1964; Ender, et al., 1968; Crosby, et al., 1972). The nitrosamines are selectively hepatotoxic while the nitrosamides damage the gastrointestinal tract, the blood forming organs and the lymphoid system (Ridd, 1961).

The effect of acid rainfall on drinking waters throughout the United States would be highly variable based upon the present pH of the water. In some areas such as the southwest the drinking water is highly alkaline and the acid rainfall would tend to neutralize the water. On the other hand, in areas like New England where the water is already acid the increased acidity of the water might well cause corrosion and the release of metals into the drinking water which could cause some serious health problems.

The interface of acid aerosols in ambient air with soil and water deserves much more study.

However, control measures directed toward controlling levels of acid aerosols in ambient air to control the public health should have a profound effect on controlling the problems of acid rainfall.

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DISCUSSION SESSION ON THE PHENOMENON

John Hawley*, Discussion Leader
James Galloway**, Rapporteur

The fact that abnormally acidic precipitation is falling on most of the eastern United States was well documented by Dr. Gene E. Likens of Cornell University. He explained that acid precipitation is caused by the strong acids, sulfuric and nitric, formed from the combustion products of fossil fuels. He also showed that there has been a thirty-six percent increase over the last ten years in the input of acidity to the Hubbard Brook Experimental Forest in New Hampshire. He explained that this increase is primarily due to an increase in the input of nitric acid from precipitation. The discussion following his presentation dealt with a number of subsidiary points that are presented below.

Technique of Measurement of Hydrogen Ion Concentration

There were four possible methods of hydrogen ion determination discussed: pH paper, pH meter, titration, and utilization of the cation-anion balance to predict the hydrogen ion concentration. Of the four, the one that is the most inaccurate is the method of determining pH by pH paper. An error of several orders of magnitude can result from using this method, especially if small volumes, such as individual rain drops, are used. The second method, the use of a pH meter equipped with a glass electrode is probably the most common method in use today and, if done precisely, gives

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*Air Resources Division, New York State Department of Environmental Conservation, Albany, New York 12233
**Postdoctoral Associate, Ecology and Systematics, Cornell University. Ithaca, New York 14853

a good estimate of the hydrogen ion concentration of the sample. The third method is essentially an extension of the second, in that one begins by determining the initial pH with the pH meter, and continues with the incremental addition of a strong base (e.g., NaOH) while monitoring the pH. This procedure (titration) can give information on the possible contribution of weak acids and bases to the total acidity of the sample. The last method, estimation of pH by a cation-anion balance is an accurate method only if the analytical procedures used to determine the concentrations of the anions and cations are accurate. It is especially useful when the detailed chemical composition of the sample is known but not the pH.

Background

Little is known about the background (natural) concentration of any of the chemical constituents of precipitation. The difficulty of the determination of these background values is because of the wide spread effect that man's activities have had on the global environment. It was agreed that a continuing effort should be made to estimate the background values for the chemical compounds in precipitation.

Sampling of Precipitation for Chemical Analysis

The question was raised as to the best way for sampling precipitation for chemical analysis. In response to this, Dr. James Galloway of Cornell University presented some guidelines on sampling which are the result of an intercalibration program involving thirteen different designs of precipitation collectors. The results presented are as follows:

1. For the determination of pH and most of the inorganic ions, plastic collectors that sample only rain or snow should be used. The use of a bulk sampler (which collects dry deposition in addition to rain and

snow) will contaminate the sample due to the inclusion of dry deposition.

2. Glass collectors are required for the determination of organic compounds.

3. For the determination of trace and heavy metals in precipitation, the collectors should be made entirely of plastic. This is because of the strong possiblity of contamination due to the low concentrations of the metals in precipitation.

4. It is best to sample the collectors after every storm, so as to avoid changes in the chemical composition of the precipitation. This is especially true if the pH of the sample is above 5. However, if the precipitation pH is less than 4.6, the collections may be sampled on a weekly basis.

Precipitation Networks

The necessity of monitoring the chemistry of precipitation in the United States was agreed upon. However, the problems of what parameters to measure and how to standardize analytical techniques are more complex. Providing that answers are forthcoming to those questions, it was agreed that the primary factor as to the size and the complexity of the network would be a financial one.

Correlation of Atmospheric Chemistry and Precipitation Chemistry

It was asked whether, knowing the concentration of the chemicals in the atmosphere, the concentration of the chemicals in the precipitation can be predicted. It was the consensus of the meeting that this is not possible on a quantitative scale at this time. However, rain chemistry can be used as an indicator of air quality.

DISCUSSION SESSION ON THE ECOLOGICAL EFFECTS

Jay Jacobson*, Discussion Leader
Don Charles** Rapporteur

At the outset Dr. Jacobson suggested that we divide the discussion period to allow discussion of three basic topics:

1. Questions on Dr. Schofield's presentation this morning.
2. Research needs on the effects of acid precipitation.
3. What is known and what is not known about the acid rain phenomenon.

TOPIC I
(Discussion of Dr. Schofield's Presentation)

Dr. Schofield indicated that effects on fish larvae of low pH have been noted in laboratory studies, but that these studies have not tried to isolate the particular mechanisms involved.

Dr. Schofield was asked why the higher lakes in the Adirondacks seem to be more susceptible to increases in acidity.

He indicated this was because there was not as great an input of cations to those lakes relative to the input of anions (primarily sulfates) and that this was due primarily to the soils and geology of the higher watersheds and the ratio of the watershed area to the lake surface area.

Dr. Schofield indicated that he had not found any variation in pH or acidity in rainfall falling on different geographical areas of the Adirondacks. He also indicated that the Department of Environmental

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*Plant Physiologist, Boyce Thompson Institute, Yonkers, New York 10701
**Project Analyst, Adirondack Park Agency, Ray Brook, New York 12977

Conservation and Cornell have done some liming of lakes, and that this liming has resulted in an increase in fish productivity. Additional changes in the lakes' ecosystems have not been studied to any great extent. He also indicated that acid resistant strains of fish, primarily brook trout,have been identified, and that there are generally differences in populations of brook trout in terms of their resistance to acidity. As yet, a determination as to whether in fact these are true genetic differences has not been made. Dr. Schofield felt that most of the fish that occur in Adirondack waters are susceptible to low pH.

In response to a question as to how well the relationship between the loss of fish in lakes and inputs of acid precipitation is established, Dr. Schofield answered that the subject definitely needs further study and that one of the best ways to do this would be to perform a detailed materials budget for lakes to determine exactly what materials, including sulfur and nitrogen, were entering the lakes and from what sources (the atmosphere or from within the watershed) they came.

The question was asked whether there are additional explanations for the decreases in acidity in Adirondack waters other than increased inputs of strong acids from the atmosphere. It was felt that there may be certain cases -- a natural bog lake, for instance -- where the natural organic acids have caused the pH to be low, but that in many, many other cases the only reasonable, most probable, explanation was that the lakes were acid because of atmospheric inputs of acids.

Then there was a discussion as to how acid effects in lakes might vary with different successional stages of lakes. Dr. Hultberg indicated that in Sweden the lakes in a later stage of succession were more susceptible to changes due to acid precipitation, probably because of the

oligotrophication (opposite of eutrophication) effects due to the changes in vegetation in the lakes in later stages. He summarized some of the effects he had found in the lakes he had studied: new invasion of macrophytes, particularly sphagnum mosses; extensions of dense fungal mats over the bottom sediments, and others.

The question was raised as to the possible effects of acid precipitation on eutrophication. Dr. Fuhs suggested that at least in terms of algal productivity in the Adirondacks, where most of the lakes are limited by phosphorus, increased inputs of nitrogen year around may affect the natural nitrogen limitations that previously occurred in the lakes. Briefly, in certain lakes in the Adirondacks blue-green algae appear in late summer, and their populations are generally limited by phophorus. However, when nitrogen supplies also become low these species, to the exclusion of all others, are capable of producing their own nitrogen, and so are able to become the dominant species at that particular time. If there were increases in nitrogen inputs, then the more desirable species of algae might be able to compete with the blue-greens and exist throughout the summer. The magnitude of the shift to blue-green algae that sometimes occurs would not be as great. This was essentially a hypothesis based on theory alone, and was suggested as a topic for further study.

TOPIC II
(Research Needs on the Effects of Acid Precipitation)

The next topic of discussion dealt with those aspects of the precipitation phenomenon which people felt deserved further study. I've already mentioned the fact that Dr. Schofield thought that there should be very detailed studies of at least one or two Adirondack lakes to

determine nutrient materials budgets. He also mentioned that the Fisheries Research Board of Canada is planning to acidify a lake with known quantities of acid and study what occurs in the lake ecosystem as a result.

Dr. Fuhs suggested that we need to know more about what happens to rain after it falls on a watershed, in its travels to various water bodies; in what ways is that precipitation modified?

One person suggested that we sould carry out laboratory studies on the effect of low pH on organisms sensitive to low pH's to determine under what conditions and by what mechanisms they are affected. The studies should be designed to determine what synergistic and antagonistic effects there might be with heavy metals.

It was suggested that more work needs to be done on the effects of acid precipitation on soil systems including the microorganisms which inhabit them. More needs to be known about the effects of acid precipitation on terrestrial ecosystems including forests and wetlands.

Dr. Likens mentioned a recently completed thesis of one of his students, Charles Cogbill, in which he looked very carefully at a number of forested areas, including the Huntington Forest in New York State, a variety of New England forests, the Smokey Mountains, and some others. Cogbill found rather consistently in most species he looked at that there was indeed a significant decline in forest growth over the past twenty years, particularly birch, in some areas. He also found that there was no way to relate this decline exclusively to any effect of acid precipitation, that there were similar declines in the past noted from radial increment growth rings, and that if one examined climate drought and things of this sort, it was impossible to state that the effects of

acid precipitation were a causative agent in forest decline and forest growth. On the other hand he was unable to state that it wasn't an effect of acid precipitation. I think this is an area that is in utmost need of further research.

It was pointed out that very little has been done on the effects of acid precipitation on agricultural crops. But this is perhaps because in many cases agricultural lands are limed anyway, and because they are more intensively managed they could be treated economically. Therefore the potential for significant adverse effects on agricultural crops is probably not as great as effects on forests.

Hans Hultberg felt that, as a subject of continuing and further research, we should define all oligotrophication processes (those involved in the self-acceleration processes causing increasing acidity). These should be studied with special reference to the time required for lakes to recover once excessive acid inputs are reduced or stopped. What recovery problems may occur if we let lakes become too acid, too long?

TOPIC III

(What is and is not known about the Acid Precipitation Phenomenon)

The consensus of the group was that there did appear to be an acid precipitation phenomenon, and that it deserved further study. There was agreement that acid precipitation is falling on ecosystems and that this precipitation is causing changes in those ecosystems. These changes have been documented in areas such as Scandanavia, the Canadian Shield, and the Adirondacks.

There was general agreement that in the Adirondacks the atmosphere is the most important source of acid affecting aquatic ecosystems; however

it was felt that some acids may originate in, and be coming from the watershed. More study needs to be done to determine relative contributions of these two inputs.

There was discussion as to how much atmospheric sulfur originates from biological sources and how much comes from man-made sources. There was general feeling that this subject required further study.

A determination of the precise kinds and physical location of sources of acid precipitation affecting a particular geographical area needs, perhaps, more study than any other subject. In terms of deciding whether or not additional control strategies should ever be implemented and what those control strategies might be would depend on this type of information perhaps more than any other.

Dr. Fuhs formulated a series of question statements he felt put acid precipitation into persepective as an environmental problem. He first stated that there was very satisfactory documentation that acid precipitation was falling in Scandanavia and that it was having substantial adverse impacts on aquatic ecosystems. He then asked whether there are inputs to the atmosphere in the United States of acid causing substances comparable to those documented in Sweden. The question was answered affirmatively. It was felt also that there have been preliminary changes in ecosystems in the U.S. that are at least similar to those documented in Scandanavia and that we can expect that if inputs in the U.S. continue we may find more effects similar to those which have occurred in Scandanavia.

DISCUSSION SESSION ON HEALTH EFFECTS

Donald Casey*, Discussion Leader
Walter Lynn**, Rapporteur

The health effects discussion group concerned itself with a number of topics which it believes should be pursued in order to better understand and evaluate the possible health effects associated with Acid Precipitation. Among these are:

1. Improve our understanding of the relationship between ambient atmospheric conditions, which currently include sizeable amounts of atmospheric pollutants and precipitation events which reflect the concentrations and the quality of ambient air.

2. There appears to be reasonably gross indices of association between atmospheric pollutants (esp. SO_4), but there is need for greater specificity in these relationships.

3. It's important to develop better health indicators in order that one can more authoritatively evaluate the effects of acid precipitation and air pollutants: for example, physiological indicators (such as asthmatics) and biological indicators should be explored.

4. There is a definite need for establishing a long-term cohort study of a sizeable population in order to evaluate the long-term effects of air pollution and acid precipitation.

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* Chief, IFYGL Branch, Rochester Field Office, U.S. Environmental Protection Agency, Rochester, N.Y. 12746.

**Director, Center for Environmental Quality Management, Cornell University, Ithaca, N.Y. 14853.

5. In order to study and to understand the health effects it will be necessary to establish very strong collaborative groups of disciplines in order to find answers to these questions.

PARTICIPANTS

Kurt Anderson
New York Power Pool
3890 Carman Road
Schenectady, New York 12303

Ross H. Arnett, Jr.
Biological Research Institute
of America
Rensselaerville, New York 12147

Connie Bart, Science Writer
Cornell News Bureau
Cornell University
110 Day Hall
Ithaca, New York 14853

Stephen Baruch
Edison Electric Institute
90 Park Avenue
New York, New York 10016

Karen M. Beil
The Conservationist
NYS Department of Environmental
Conservation
5 Lincoln Avenue
Albany, New York 12205

Michael Berry
Office of Air Quality Planning
and Standards
Environmental Protection Agency
Research Triangle Park,
North Carolina 27711

David E. Buerle
Catskill Study Commission
Rexmere Park
Stamford, New York 12167

Donald J. Casey, Chief
U.S. Environmental Protection
Agency,Rochester Field Office
P. O. Box 5036
Rochester, New York 12746

Donald Charles
Adirondack Park Agency
P. O. Box 99
Ray Brook, New York 12977

Peter E. Coffey
Dept. of Environmental
Conservation
50 Wolf Road
Albany, New York 12233

Robert L. Collin, Director of
Environmental Management
Monroe Co. Environ.Mgt.Council
39 Calumet Street
Rochester, New York 14610

Robert Craig
Adirondack Park Agency
P. O. Box 99
Ray Brook, New York 12977

Raymond Curran
Adirondack Park Agency
P. O. Box 99
Ray Brook, New York 12977

Robert C. Dalgleish, Director
The E.N. Huyck Preserve and
Biological Station
Rensselaerville, New York 12147

Valentine J. Descamps
Environmental Protection Agency
Region I
255 Weston Road
Wellesley, MA 02181

Michael Dick, Senate Aid
c/o Senator B. Smith, Chairman
Senate Committee on Conservation
Recreation and the Environment
NY State Senate
State Capitol Building
Albany, New York 12224

PARTICIPANTS

Steve Eabry
Office of Environmental Planning
Public Service Commission
44 Holland Avenue
Albany, New York 12208

Thomas Eichler, Director
Program Development, Planning & Research
New York State Department of Environmental Conservation
Room 422, 50 Wolf Road
Albany, New York 12233

Raymond E. Falconer
Atmospheric Sciences Research Center, SUNY at Albany
9 Townley Drive
Burnt Hills, New York 12021

Peter Foley
Mobil Oil
150 East 42nd Street
New York, New York 10017

Arnold Freiberger
U.S. Environmental Protection Agency, Region II, Rm. 302
26 Federal Plaza
New York, New York 10007

Jean G. French
Human Studies Laboratory
National Environmental Research Center
Environmental Protection Agency
Research Triangle Park
North Carolina 27711

Peter Freudenthal
Chief Air Quality Engineer
Consolidated Edison
4 Irving Place
New York, New York 10003

John A. Fizzola
Suffolk County Department of Environmental Control
1324 Motor Parkway
Hauppauge, New York 11787

G. W. Fuhs
Division of Laboratories & Research
N.Y.S. Department of Health
New Scotland Avenue
Albany, New York 12201

Howard I. Fuller
United Kingdom Institute of Petroleum
61 New Cavendish Street
London W1, United Kingdom

James J. Galloway
Ecology & Systematics Division
Cornell University
277 Langmuir Lab.
Ithaca, New York 14853

Olle Grahn
The Swedish Water & Air Pollution Research Lab.
Sten Sturegatan 42
Gothenburg 5, Sweden

Frederick W. Hardt
Environmental Associates
Wing Road
Rexford, New York 12148

Thomas E. Harr
Environmental Quality Research Unit
N.Y.S. Department of Environmental Conservation, 50 Wolf Road
Albany, New York 12233

PARTICIPANTS

John Hawley
N.Y.S. Department of Environmental Conservation
50 Wolf Road
Albany, New York 12233

John Heidelberger
c/o Senator B. Smith
Senate Committee on Conservation, Recreation and the Environment
N.Y. State Senate
State Capitol Building
Albany, New York 12208

Lawrence Heller
Boyce Thompson Institute
1086 North Broadway
Yonkers, New York 10701

William P. Hofmann
N.Y.S. Department of Transportation
1220 Washington Avenue
Albany, New York 12232

Hary Hovey, Associate Director
Division of Air Resources
N.Y.S. Department of Environmental Conservation
50 Wolf Road
Albany, New York 12233

Hans Hultberg
The Swedish Water & Air Pollution Research Lab.
Sten Sturegatan 42
Gothenburg 5, Sweden

William T. Ingram
Environmental Engineering
Cornell University Medical College
1300 York Avenue, Room A630
New York, New York 10021

Jay S. Jacobson
Boyce Thompson Institute
1086 North Broadway
Yonkers, New York 10701

Kenneth Juris
New York Power Pool
3890 Carman Road
Schenectady, New York 12303

John Kadlecek
Atmospheric Science Research Center
130 Saratoga Road
Scotia, New York 12302

Shigeru Kobayashi, Lab Director
Rensselaer Fresh Water Institute
Rensselaer Polytechnic Institute
Troy, New York 12180

Gilbert Levine, Director
Water Resources & Marine Sciences Center
Cornell University
468 Hollister Hall
Ithaca, New York 14853

Gene E. Likens, Professor
Ecology & Systematics
Cornell University
221 Langmuir Laboratory
Ithaca, New York 14853

Walter R. Lynn, Director
Center for Environmental Quality Management
Cornell University
468 Hollister Hall
Ithaca, New York 14853

PARTICIPANTS

Robert W. Mason
Region II, U.S. Environmental
Protection Agency
26 Federal Plaza
New York, New York 10007

Robert Means
N.Y.S. Science Service
State Education Department
State Education Building
Albany, New York 12223

Volker A. Mohnen, Acting Director
Atmospheric Sciences Research
Center, SUNY at Albany
Rm. ES 319
1400 Washington Avenue
Albany, New York 12206

Andrew Montz
Office of Environmental Planning
N.Y.S. Department of Public
Service
44 Holland Avenue
Albany, New York 12208

Margaret B. Neno
Center for Environmental Quality
Management
Cornell University
468 Hollister Hall
Ithaca, New York 14853

Joseph M. O'Connor
A.J. Lanza Laboratories
Department of Environmental
Medicine
New York University
Long Meadow Road
Tuxedo, New York 10987

Svante Oden
Division of Ecochemistry
Agricultural College
750 07 Uppsala, Sweden

Eric Outwater, Deputy Regional
Administrator
Region II, U.S. Environmental
Protection Agency
26 Federal Plaza
New York, New York 10007

Herbert Posner, Chairman
Assembly Environmental
Conservation Committee
N.Y.S. Assembly
State Capitol
Albany, New York 12224

Lyle S. Raymond, Jr.
Cooperative Extension
Cornell University
473 Hollister Hall
Ithaca, New York 14853

Boyce Rensberger
New York Times
229 West 43rd Street
New York, New York 10036

H.G. Richter
U.S. Environmental Protection
Agency
Research Triangle Park
North Carolina 27709

Richard B. Ruch, Jr.
Senior Environmental
Meteorologist
Environmental Analysts, Inc.
224 Seventh Street
Garden City, New York 11530

Vincent J. Schaefer
Atmospheric Sciences Research
Center, SUNY at Albany
R.D. 3, Box 36
Schenectady, New York 12306

PARTICIPANTS

Carl L. Schofield
Natural Resources Department
Cornell University
Fishery Laboratory
Ithaca, New York 14853

Sidney Schwartz, Director
N.Y.S. Department of Environmental
Conservation, 50 Wolf Road
Albany, New York 12233

Janine Selendy, Editor
N.Y.S. Environment
N.Y.S. Department of Environmental
Conservation, Rm 602
50 Wolf Road
Albany, New York 12233

J. Douglas Sheppard
Supervising Aquatic Biologist
Bureau of Fisheries
N.Y.S. Department of Environmental
Conservation, 50 Wolf Road
Albany, New York 12233

Herschel Slater, Chief
Source Receptor Analysis Branch
Office of Air Quality Planning
and Standards
Environmental Protection Agency
Research Triangle Park
North Carolina 27711

Patrick Smyth
Temporary State Commission on
Tug Hill
State Office Building
Watertown, New York 13601

Gerald Soffian
Environmental Protection Agency
Room 905B
26 Federal Plaza
New York, New York 10007

Joseph Spatola, Chief
Air Monitoring Section
Surveillance & Monitoring
Branch
Surveillance & Analysis
Division
Region II, U.S. Environmental
Protection Agency
Edison, New Jersey 08817

William Stasiuk
N.Y.S. Department of
Environmental Conservation
30 Pheasant Lane
Delmar, New York 12054

Gary Stensland
Department of Chemistry &
Environmental Engineering
North Hall
Rensselaer Polytechnic
Institute
Troy, New York 12180

Glenn Stevenson
Scientific Advisory Staff
N.Y. State Legislature
Albany, New York 12224

Vic Stewart, Reporter
Knickerbocker Press
Albany, New York 12201

Diane Stoecker, Assistant Director
Terrestrial Ecology
Environmental Analysts, Inc.
224 Seventh Street
Garden City, New York 11530

Gary Toenniessen, Assistant Director
Quality of the Environment
Program, Rockefeller Foundation
1133 Avenue of the Americas
New York, New York 10036

PARTICIPANTS

Donald White
Cornell University Regional
Office
Martin Road
Voorheesville, New York 12186

Robert Williams
Institute for Public Policy
Alternatives
99 Washington Avenue
Albany, New York 12210

Sherman Williams, Manager
Health & Environmental
Protection
General Electric Company
P.O. Box 1072
Schenectady, New York 12303

Charles Wolf, Manager
N.Y.S. Electric & Gas Corporation
4500 Vestal Parkway East
Binghamton, New York 13902

George Wolff
Interstate Sanitation Commission
10 Columbus Circle
New York City, New York 10019

PROGRAM

MONDAY, MAY 19, 1975

5:30 - Welcoming Gathering and
6:30 - Cash Bar

6:30 - Dinner

Presider - Sidney Schwartz
Director of Research
N.Y.S. Department of Environmental Conservation

Welcome - Herbert Posner, Chairman
Assembly Environmental Conservation Committee

Keynote Address -

Acid Precipitation: A World Concern

Svante Odén, Professor
Division of Ecochemistry
Agricultural College
Uppsala, Sweden

TUESDAY, MAY 20, 1975

9:00 - Plenary Session I

Presider - Gilbert Levine, Director
Water Resources & Marine Sciences Center
Cornell University

Our Understanding of the Phenomenon

Gene Likens, Professor
Ecology and Systematics
Cornell University

Our Understanding of the Ecological Effects

Carl Schofield
Sr. Research Associate
Natural Resources
Cornell University

Our Understanding of the Health Effects

Jean French, Epidemiologist
Human Studies Laboratory
National Environmental Research Center
Environmental Protection Agency
Research Triangle Park, North Carolina

(Break)

12:00 - Lunch

1:00 - Plenary Session II

Presider - Walter Lynn, Director
Center for Environmental Quality Management
Cornell University

Speakers - Commissioner Ogden Reid
N.Y.S. Department of Environmental Conservation

Eric Outwater
Regional Administrator
Region II
U.S. Environmental Protection Agency

2:00 - Discussion Sections

1. The Phenomenon

Discussion Leader -
John Hawley, Air Resources
N.Y.S. Department of Environmental Conservation

Rapporteur -
James Galloway
Postdoctoral Associate
Ecology and Systematics
Cornell University

2. Ecological Effects

Discussion Leader -
Jay Jacobson
Plant Physiologist
Boyce Thompson Institute

Rapporteur -
Donald Charles
Project Analyst
Adirondack Park Agency

3. Health Effects

Discussion Leader -
Donald Casey, Chief
IFYGL Branch, Rochester Field Office
Environmental Protection Agency

Rapporteur -
Walter Lynn

(Break)

3:30 - Plenary Session III

Presider - Arnold Freiberger
Research Representative
Region II
Environmental Protection Agency

Reports from Discussion Speakers

4:30 - Adjourn